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From antiquity to the early nineteenth century

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Author of *The Scientific Work of René Descartes* (1596–1650),

Mathematical Work of John Wallis, D.D., F.R.S. (1616–1703), and other works

CONTENTS: Mathematics in Antiquity—Greek Mathematics—The Invention of Trigonometry—Decline of Alexandrian Science and the Revival in Europe—Mathematics in the Orient—Progress of Mathematics during the Renaissance—New Methods in Geometry—The Rise of Mechanics—The Invention of Decimal Fractions and of Logarithms—Newton and the Calculus—Taylor and Maclaurin, the Bernoullis and Euler, Related Advances—The Calculus of Variations, Probability, Projective Geometry, Non-Euclidean Geometry—Theory of Numbers—Lagrange, Legendre, Laplace, Gauss. This volume is intended primarily to help students who desire to have a knowledge of the development of the subject but who have too little leisure to consult works and documents. The author has availed himself of the facilities afforded by the Royal Society and other learned Societies to reproduce extracts from manuscripts and many scarce works.

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On the Theory of Cooperative Phenomena in Crystals

[Continued from Vol. 9, No. 34, p. 244, April 1960]

By C. Domb

King's College, Strand, W.C.2

§ 4. APPROXIMATE METHODS

4.1. *Introduction*

The approach which we have used so far in the theory of cooperative phenomena has not followed the historical development of the subject. Approximate methods had been widely used for several years before any exact information on two-dimensional models, which we have discussed in the previous chapter, became available. The simplest approximation, usually referred to as zeroth order, was used by Bragg and Williams (1934) in a discussion of order-disorder transitions in alloys. It introduced for the first time the concept of long-range order, and with relatively simple mathematics seemed to account for the main features of the experimental results. The Curie temperature was characterized by the disappearance of long-range order, and was associated with a specific heat singularity. The form of the predicted singularity was not in complete accord with experiment, the most unsatisfactory feature being the drop of the specific heat to zero above the Curie temperature.

In 1935 Bethe introduced an improved approximation (usually referred to as a first-order approximation) which took account of short-range order as well as long-range order; the specific heat curve derived from this approximation did not fall to zero above the Curie temperature, but a small 'tail' remained, and this was in better agreement with experiment. The approximation was applied by Peierls (1936) to the Ising model, and independently Guggenheim (1935) developed an approximation of comparable order which he applied to the theory of regular solutions.

The exact approach to the two-dimensional Ising model by Kramers and Wannier in 1941, and the complete solution in the absence of a magnetic field by Onsager in 1944 showed clearly the limitations of the above approximations in predicting behaviour in the neighbourhood of the Curie point. In fact the exact solution depended on an infinity of order parameters, whereas the approximations took account of only one or two of them. The form of the specific heat curve in Onsager's solution differed substantially from those obtained by the approximations, but differed equally markedly from experimentally observed specific heat curves. Perhaps the most striking difference was the large 'tail' of the Onsager curve, which showed that a substantial fraction of the total entropy change of the system took place in the temperature region above the Curie point. It was therefore important to determine whether this behaviour arose from the two-dimensional nature of the model, and how it was modified for a three-dimensional model

We have already pointed out that the methods used in the previous chapter for deriving exact solutions depend on particular properties of two-dimensional nets, and cannot be generalized to three dimensions. In the years which elapsed after the appearance of Onsager's solution, despite several claims, no real progress was made towards an exact solution of a three-dimensional model; the problem seems to be one of outstanding difficulty. However, higher order approximations in closed form were developed and systematic methods were devised of obtaining terms of the series expansions discussed in § 3.6.

The literature on such approximations is very extensive, and it has not been practicable to give a detailed account of all the different approaches which have been used. We have, instead, selected those which seemed to us to be the most significant, for detailed consideration, and have endeavoured to summarize the remainder. Reliable information regarding the true thermodynamic properties of a given model can best be obtained from a series of successive approximations, which enable one to assess the general trend of a particular property and hence to estimate the error involved in stopping at a particular stage. Unfortunately the labour arising in such approximations increases rapidly with the order of the approximation, and the process cannot usually be followed for more than 2 or 3 stages.

Exact series expansions have been developed quite extensively; when they converge might up to the critical region they can usually provide useful and reliable information. When they do not converge in the critical region some re-arrangement of the terms must be sought, and approximations in closed form can be a useful guide to the asymptotic behaviour of the series.

By combining information obtained from series expansions and higher order approximations in closed form, we believe that most of the important properties of the three-dimensional model can be reliably established, and we give an account of these properties in § 4.7. We should then be in a better position to compare the results with experiment, and to see whether a serious refinement of the model is needed to secure effective agreement.

4.2. *Zero Order Approximations*

The first attempt to account in detail for the properties of a ferromagnetic was made many years ago by Pierre Weiss (1907) who postulated the existence of a large 'internal field'. Using this hypothesis Weiss was able to reproduce the most important physical features of a ferromagnetic, the existence of a Curie temperature, of a spontaneous magnetization below the Curie temperature, and the form of the susceptibility curve above the Curie temperature. However, the origin of the 'internal field' was not discussed in detail, and thus a statistical formulation in terms of atomic interactions was not possible. In 1925 Ising attempted such a formulation, although the form of interaction which he took was somewhat empirical. In 1928 Heisenberg gave a quantum mechanical

which is equivalent to the equation derived by Weiss (1907).

In the absence of an external field equation (4) may be written

$$\tanh \xi = \frac{kT}{qJ} \xi \quad (\xi = mH_0/kT). \quad (5)$$

From fig. 1 it will be seen that when $kT/qJ > 1$ the only solution is $\xi = 0$; but when $kT/qJ < 1$ there are two additional equal and opposite non-zero solutions for ξ . The magnetization is given by

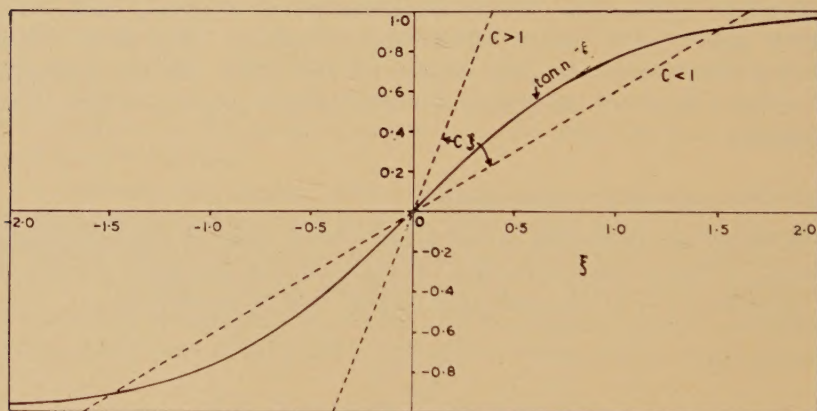
$$I = m(\alpha_2 - \alpha_1) = \frac{m^2}{qJ} H_0, \quad (6)$$

and hence a non-zero value of ξ in zero external field corresponds to the existence of a spontaneous magnetization. We must first prove that this non-zero value of ξ gives rise to the lowest free energy; this can be shown more readily by the approach in the next section.

The Curie temperature corresponds to the appearance of a non-zero solution for ξ in (5), and is given by

$$\frac{kT_c}{qJ} = 1. \quad (7)$$

Fig. 1



Condition for the existence of a spontaneous magnetization in the mean field approximation. When $C > 1$ the only solution of $\tanh \xi = C\xi$ is $\xi = 0$; when $C < 1$ there are two additional solutions ($C = kT/qJ$).

The form of the spontaneous magnetization can be calculated from (5) and (6). For low temperatures (ξ large)

$$I_0 \simeq m[1 - 2 \exp(-2qJ/kT)]; \quad (8)$$

but near the Curie temperature (ξ small)

$$I_0 \simeq m \left[3 \left(1 - \frac{T}{T_c} \right) \right]^{1/2}. \quad (9)$$

The susceptibility is given by $(\partial I/\partial H)$ and can readily be calculated from (4) and (6). We have,

$$\begin{aligned} (\partial H_0/\partial H)/qJ &= \text{sech}^2 [m(H + H_0)/kT][1 + (\partial H_0/\partial H)]/kT \\ &= [I + (\partial H_0/\partial H)]/kT[1 - (mH_0/qJ)^2]. \end{aligned} \quad (10)$$

The susceptibility in zero field for $T > T_c$ is obtained by putting $H_0 = 0$ in (10); we derive the Curie-Weiss law

$$\chi_0 = \frac{m^2}{qJ} \left(\frac{\partial H_0}{\partial H} \right)_{H=0} = m^2/k(T - T_c), \quad (11)$$

for which the inverse susceptibility is exactly linear.

It should be noted that thermodynamic quantities in this approximation depend only on T/T_c , and hence are the same for all lattices. The approximation is completely wrong for a linear chain ($q = 2$) since we know that there is no singularity in this case (§ 3.1). It is somewhat better for the two-dimensional lattices improving steadily with increasing coordination number; from § 3 eqn. (183) the values of kT_c/qJ for the honeycomb, quadratic, and triangular lattices are 0.506, 0.567, 0.607 respectively.

There is no difficulty in generalizing the approximation to take account of distant neighbour interactions. The only change is in the Curie temperature (7) which is now given by

$$kT_c = q_1 J_1 + q_2 J_2 + \dots q_r J_r. \quad (12)$$

4.2.2. The approximation of random mixing

Let us consider all configurations with N_1 spins pointing in direction 1 and N_2 in direction 2. There are $N!/(N_1! N_2!)$ such possible configurations, and when the positions of these spins in the lattice are completely random, the mean number of 1-2 nearest neighbour pairs is

$$\langle N_{12} \rangle = 2 \frac{N_1}{N} \frac{N_2}{N} (qN/2) = qN_1 N_2 / N. \quad (13)$$

Our approximation is to assume that formula (13) holds even when there are interactions between the spins, so that we ignore correlations between neighbouring atoms. We can now write down the free energy for the Ising model (§ 2 eqns. (5), (9)), replacing N_{12} by its mean value from (13),

$$\left. \begin{aligned} F_N^I &= -N m H - \frac{qN}{2} J - kT \ln \Lambda_N(\mu, z), \\ \Lambda_N(\mu, z) &= \sum_{N_1 + N_2 = N} \frac{N!}{N_1! N_2!} \mu^{N_1} z^{qN_1 N_2 / N}. \end{aligned} \right\} \quad (14)$$

For large N we can as usual replace the sum in (14) by its maximum term. The logarithm of the general term is asymptotically equal to

$$N \ln N - N_1 \ln N_1 - N_2 \ln N_2 + N_1 \ln \mu + \frac{qN_1 N_2}{N} \ln z; \quad (15)$$

differentiating with respect to N_1 ($N_2 = N - N_1$), we obtain for the maximum term the equation

$$-\ln N_1 + \ln N_2 + \ln \mu + q \frac{(N_2 - N_1)}{N} \ln z = 0. \quad (16)$$

Writing $N_1 = N(1 - \delta)/2$, $N_2 = N(1 + \delta)/2$ we obtain

$$\frac{1 + \delta}{1 - \delta} = \frac{2mH}{kT} + \frac{2qJ}{kT}, \quad \dots \quad (17)$$

which is exactly equivalent to (4). Thus when $H = 0$, for $T > T_c$ (15) has only one stationary value which corresponds to $\delta = 0$, or random orientation and mixing of spins. But when $T < T_c$ (15) has three stationary values. Differentiating the left-hand side of (16) we obtain for the second derivative of a typical term

$$-\frac{1}{N_1} - \frac{1}{N_2} + \frac{4qJ}{NkT} = \frac{2}{N} \left[-\frac{1}{1 + \delta} - \frac{1}{1 - \delta} + \frac{2T_c}{T} \right]. \quad (18)$$

Hence when $T > T_c$ the stationary value at $\delta = 0$ is a maximum; but when $T < T_c$ the stationary value at $\delta = 0$ is a minimum, and the non-zero values given by (17) are maxima.

We can now replace $\Lambda_N(\mu, z)$ by its maximum term given by (17) and (15), and hence derive the values of any thermodynamic functions in this approximation. Thus when $H = 0$ the internal energy is given

$$E_N^I = -\frac{qN}{2}J + 2q\frac{N_1N_2}{N}J = -\frac{qNJ\delta^2}{2}. \quad (19)$$

Hence we derive the following approximations for the internal energy:

$$\left. \begin{aligned} T \ll T_c, \quad E_N^I &\simeq -\frac{NqJ}{2} [1 - 4 \exp(-2T_c/T)], \\ T_c - T \text{ small} \\ \text{and positive,} \quad E_N^I &\simeq -\frac{3qNJ}{2} \left[\left(\frac{T_c}{T} - 1 \right) - \frac{9}{5} \left(\frac{T_c}{T} - 1 \right)^2 \right], \\ T > T_c, \quad E_N^I &= 0. \end{aligned} \right\} \quad (20)$$

For the specific heat we have similarly

$$\left. \begin{aligned} T \ll T_c, \quad C_v &\simeq Nk \left(\frac{2T_c}{T} \right)^2 \exp(-2T_c/T), \\ T_c - T \text{ small} \\ \text{and positive,} \quad C_v &\simeq \frac{3}{2} Nk \left[1 - \frac{8}{5} \left(\frac{T_c}{T} - 1 \right) \right], \\ T > T_c, \quad C_v &= 0. \end{aligned} \right\} \quad (21)$$

It was noted by Bell (1952) that inconsistent results arise if the partition function is constructed using the mean field of the previous section and treating it in the same manner as an external field; the simplest method of obtaining a consistent partition function is the use of a combinatorial factor as in the present section.

4.3. First-order Approximations

Both of the approaches of the previous sections have their natural generalizations to an improved approximation. The mean field approximation leads naturally to the Bethe approximation which treats more accurately the interaction of a given spin with its nearest neighbours. Improvement of the approximation of random mixing leads to the quasi-chemical approximation. For the Ising model the results of the improved

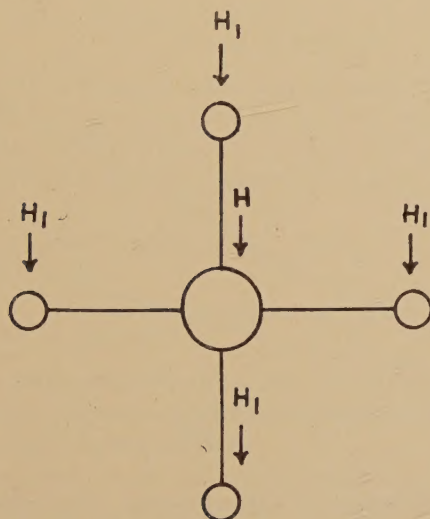
approximations are mathematically identical; however, we shall again give a brief account of both approaches, observing that the extension of the approximations to higher order, and to the Heisenberg model, no longer produces identical results.

4.3.1. The Bethe approximation

The Bethe approximation takes exact account of the interaction of a given spin with its nearest neighbours, but uses a 'mean field' to take account of the interactions of these neighbours with other spins of the lattice (fig. 2). The energy of interaction of an elementary cluster consisting of the central spin and its q nearest neighbours is then

$$\mathcal{H}_q = - \sum_{j=1}^q J \sigma_{0z} \sigma_{jz} - mH \sigma_{0z} - mH_1 \sum_{j=1}^q \sigma_{jz}, \quad \dots \quad (22)$$

Fig. 2



A cluster consisting of a central spin and its nearest neighbours for the Bethe approximation. The magnetic field acting on the central spin is the external field H ; an additional field acts on the outer spins arising from the coupling with the remaining spins of the lattice.

where as before the magnetic field is taken in direction 2. The partition function for this elementary cluster is

$$\begin{aligned} Z_q &= \mu^{-1/2} (\mu_1^{-q/2} z^{-q/2} + {}^s C_1 \mu_1^{-q/2+1} z^{-q/2+1} + {}^s C_2 \mu_1^{-q/2+2} z^{-q/2+2} + \dots) \\ &\quad + \mu^{1/2} (\mu_1^{q/2} z^{-q/2} + {}^s C_1 \mu_1^{q/2-1} z^{-q/2+1} + {}^s C_2 \mu_1^{q/2-2} z^{-q/2+2} + \dots) \\ &= \mu^{-1/2} (\mu_1^{-1/2} z^{-1/2} + \mu_1^{1/2} z^{1/2})^q + \mu^{1/2} (\mu_1^{1/2} z^{-1/2} + \mu_1^{-1/2} z^{1/2})^q, \quad \dots \quad (23) \end{aligned}$$

where

$$\mu = \exp(-2mH/kT), \quad \mu_1 = \exp(-2mH_1/kT), \quad z = \exp(-2J/kT).$$

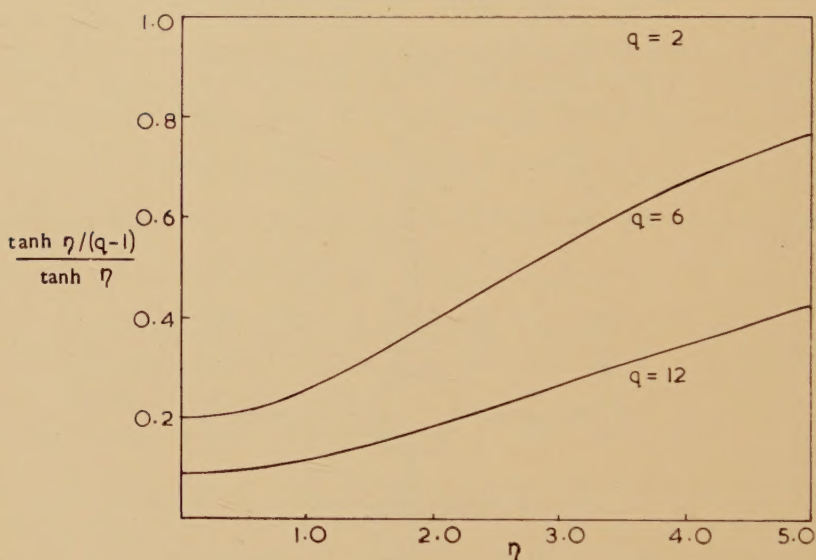
The mean field H_1 is determined by the consistency condition that the probability of a spin pointing in directions 1 and 2 is the same for the central spin or any of the outer spins. Thus

$$\mu \frac{\partial}{\partial \mu} \ln Z_q = \frac{\mu_1}{q} \frac{\partial}{\partial \mu_1} \ln Z_q. \quad (24)$$

Applying (24) to (23) we find after a little simplification

$$\frac{\mu_1}{\mu} = \left(\frac{\mu_1 + z}{1 + \mu_1 z} \right)^{q-1}. \quad (25)$$

Fig. 3



Condition for the existence of a spontaneous magnetization in the Bethe approximation. When $\tanh (J/kT) < 1/(q-1)$ there is no non zero solution for η ; when $\tanh (J/kT) > 1/(q-1)$ there is a non-zero solution ($\eta = mH_1/kT$).

In the absence of a magnetic field ($\mu = 1$), $H_1 = 0$ is always a solution. To find if a non-zero solution exists for H_1 we readily transform (25) into

$$\frac{\tanh [mH_1/(q-1)kT]}{\tanh (mH_1/kT)} = \tanh (J/kT). \quad (26)$$

We have sketched the form of $\tanh (\eta/q-1)/\tanh \eta$ in fig. 3; it starts with the value $1/(q-1)$ at $\eta=0$ and increases steadily to 1 at $\eta=\infty$. Hence at any temperature T satisfying

$$\tanh (J/kT) < 1/(q-1) \quad (27)$$

there is no non-zero solution for H_1 ; for all other temperatures the non-zero value of H_1 is given by the intersection of the curve in fig. 3 with the line $y = \tanh (J/kT)$. The Curie temperature is thus given by

$$\tanh (J/kT_c) = 1/(q-1), \quad kT_c/qJ = -\frac{2/q}{\ln (1-2/q)}. \quad (28)$$

For a linear chain $q=2$ and the Curie point is at zero temperature, as it should be. As q increases kT_c/qJ increases steadily reaching the limiting value of 1 as $q \rightarrow \infty$. In fact if in (26) we allow q to become large and J to become small, qJ remaining finite, we recover the mean field eqn. (5).

From the partition function for an elementary cluster, (23), we find that the mean fraction α_1 of spins pointing in direction 1 is given by

$$\alpha_1 = \frac{\mu^{1/2}(\mu_1^{1/2}z^{-1/2} + \mu_1^{-1/2}z^{1/2})^q}{Z_q} = \frac{\mu_1(u_1 + z)}{1 + \mu_1^2 + 2\mu_1 z}. \quad (29)$$

Using (6) and (25) we find for the magnetization

$$I = m \frac{1 - \mu_1^2}{1 + \mu_1^2 + 2\mu_1 z}. \quad (30)$$

As $H \rightarrow 0$ when $H_1 \neq 0$ we obtain a spontaneous magnetization. Near $T=0$ we can derive from (25) an expansion for μ_1 in powers of z starting with $\mu_1 = z^{q-1}$; from this we can derive a corresponding expansion for I_0 . Near $T=T_c$ it is better to use (26) and expand for small H_1 ; we find that

$$\left. \begin{aligned} (mH_1/kT)^2 &\simeq 3(q-1) [\ln q/(q-2)] \left(\frac{T_c}{T} - 1 \right), \\ I_0 &\simeq m \left\{ \frac{3q^2}{2(q-1)} [\ln q/(q-2)] \left(\frac{T_c}{T} - 1 \right) \right\}^{1/2}. \end{aligned} \right\} \quad (31)$$

Hence the spontaneous magnetization curve is steepest for small q , and becomes less steep as q increases ultimately tending to the limiting form (9) given by the mean field approximation.

The susceptibility can be obtained by differentiating I in (30) with respect to H , using (25) to obtain $d\mu_1/dH$. For the susceptibility in zero field above the Curie point we put $H=H_1=0$ after differentiation, and a substantial simplification occurs. We find that

$$\chi_0 = \frac{m^2}{kT} \frac{2}{qz - (q-2)}, \quad (32)$$

a formula first derived by Firgau (1941).

The internal energy per spin can be obtained by considering the 'bond' energy of an elementary cluster, i.e. the contribution from the interaction of nearest neighbour pairs. If we then sum over all spins of the lattice each bond will be counted twice. Hence the total 'bond' energy of the lattice is given by

$$\frac{N}{2} 2Jz \frac{\partial}{\partial z} (\ln Z_q) = -\frac{NqJ}{2} \left[\frac{1 + \mu_1^2 - 2\mu_1 z}{1 + \mu_1^2 + 2\mu_1 z} \right], \quad (33)$$

after simplification by means of (25). In the absence of an external magnetic field this is the only contribution to the energy, and we shall confine our attention to this case. For $T > T_c$, $H_1 = 0$ and we find

$$E_N = -\frac{NqJ}{2} \frac{(1-z)}{(1+z)}. \quad (34)$$

The value of the energy at the Curie point is thus

$$E_c = -NqJ/2(q-1), \quad (q > 2) \quad (35)$$

and for temperatures just above T_c

$$\left. \begin{aligned} E_N &= E_c + NJ \frac{q^2(q-2)}{4(q-1)^2} [\ln q/(q-2)] \left(\frac{T}{T_c} - 1 \right) + 0 \left(\frac{T}{T_c} - 1 \right)^2, \\ C_v &= Nk \frac{q^2(q-2)}{8(q-1)^2} [\ln q/(q-2)]^2 + 0 \left(\frac{T}{T_c} - 1 \right). \end{aligned} \right\} \quad (36)$$

Below the Curie point we must calculate μ_1 from (25) and substitute in (33). For temperatures just below T_c , expanding as in (31), we find that

$$\left. \begin{aligned} E_N &= E_c - NJ \frac{q^2(q-2)(3q-2)}{4(q-1)^2} \left(\ln \frac{q}{q-2} \right) \left(\frac{T_c}{T} - 1 \right) + 0 \left(\frac{T_c}{T} - 1 \right)^2, \\ C_v &= Nk \frac{q^2(q-2)(3q-2)}{8(q-1)^2} \left(\ln \frac{q}{q-2} \right)^2 + 0 \left(\frac{T_c}{T} - 1 \right). \end{aligned} \right\} \quad (37)$$

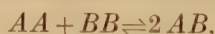
The formulae which we have derived here using the Bethe approximation are most usefully applicable to loose packed lattices in which there is no interaction between spins of the outer shell in fig. 2. For lattices such as the triangular and face-centred cubic these interactions should be taken into account in the partition function Z_q , and if they are ignored the approximation will be less accurate. The shapes of the thermodynamic functions in this approximation depend only on the coordination number q , and we shall discuss their detailed behaviour subsequently in § 4.7.

4.3.2. The quasi-chemical approximation

In 1935 Guggenheim, using the analogy of the equilibrium theory of chemical reactions, suggested an improvement of the approximation of random mixing in the theory of solutions. From (13) and analogous equations for $\langle N_{11} \rangle$ and $\langle N_{22} \rangle$ we find that in this latter approximation

$$\frac{\langle N_{12} \rangle^2}{\langle N_{11} \rangle \langle N_{22} \rangle} = 4. \quad (38)$$

However, if we consider the chemical reaction between molecules



ignoring vibrational and rotational effects, the equilibrium state is given by (Rushbrooke 1949, Chapter 11)

$$\frac{\langle N_{12} \rangle^2}{\langle N_{11} \rangle \langle N_{22} \rangle} = \frac{4[\exp(-\epsilon_{12}/kT)]^2}{[\exp(-\epsilon_{11}/kT)][\exp(-\epsilon_{22}/kT)]} \quad (39)$$

Guggenheim therefore suggested that (39) should be applied to the theory of solutions as an improvement of (38), the right-hand side of (39) being in fact equal to $4z^2$; he also proposed the term quasi-chemical to characterize the approximation.

From (39), using the fundamental relations in eqn. (2) of § 2, we easily deduce that

$$\frac{\langle N_{12} \rangle}{qN} = \frac{-z^2 + \sqrt{[z^4(1 + 4\alpha_1\alpha_2) - 4z^2\alpha_1\alpha_2]}}{2(1 - z^2)}. \quad (40)$$

Now the internal energy of a solution (fixed N_1, N_2) is given, apart from a zero energy term, by $\langle N_{12} \rangle \epsilon$ (§ 2, eqn. (3)); also

$$E_N = -kT^2 \frac{\partial}{\partial T} (\ln Z_N) = \epsilon z \frac{\partial}{\partial z} (\ln Z_N). \quad (41)$$

Hence using (40) and (41) we can integrate to find $\ln Z_N$; the constant of integration is fixed by considering the value at $z = 1$ ($T = \infty$) where random mixing occurs. We thus find that (except for zero energy terms)

$$\left. \begin{aligned} \ln Z_N = & -\frac{1}{2}qN \left[\alpha_1 \ln \frac{B + \alpha_1 - \alpha_2}{B + 1} + \alpha_2 \ln \frac{B - \alpha_1 + \alpha_2}{B + 1} \right. \\ & \left. - \frac{q-2}{q} (\alpha_1 \ln \alpha_1 + \alpha_2 \ln \alpha_2) \right] \\ & B = \sqrt{[4\alpha_1\alpha_2z^{-2} + (\alpha_1 - \alpha_2)^2]}. \end{aligned} \right\} \quad (42)$$

(Details of the calculations are given in Rushbrooke (1949), Chapter 18, § 6.)

To determine the thermodynamic behaviour at different temperatures we must plot the free energy as a function of the concentration α_1 of one of the constituents. The results obtained are equivalent to those of the Bethe approximation. Above a temperature T_c given by (28) the free energy minimum corresponds to $\alpha_1 = \frac{1}{2}$; but below T_c there are two values of α_1 , $(\frac{1}{2} + \delta)$ and $(\frac{1}{2} - \delta)$ ($\delta \neq 0$), giving rise to minima in the free energy. Below T_c the stationary value at $\alpha_1 = \frac{1}{2}$ becomes a maximum and does not correspond to a stable state. The results can then readily be re-interpreted for the Ising model.

The partition function for the Ising model for $H = 0$ at temperatures above the Curie point is readily obtained from (42) by putting $\alpha_1 = \alpha_2 = \frac{1}{2}$;

$$\ln Z_N = \frac{1}{2}qN \left[-\frac{q-2}{q} \ln 2 + \ln(1+z) \right]. \quad (43)$$

From this we can write down the critical value of the entropy

$$S_c = \frac{\partial}{\partial T} (kT \ln Z_N)_c = Nk \left[\ln 2 + \frac{q}{2} \ln \left(1 - \frac{1}{q} \right) - \frac{q(q-2)}{4(q-1)} \ln \left(1 - \frac{2}{q} \right) \right] \quad (44)$$

Subsequently, Fowler and Guggenheim (1949) (see Guggenheim (1952)) and Li (1949) developed independently an alternative approach to the quasi-chemical approximation by deriving an expression for the combinatorial factor $g(N; N_1, N_{12})$,

$$g(N; N_1, N_{12}) = \frac{(\frac{1}{2}qN)!}{N_{11}! N_{22}! [(N_{12}/2)!]^2} \left[\frac{N_1! N_2!}{N!} \right]^{q-1}. \quad (45)$$

This provides a simpler method of calculating thermodynamic functions on the quasi-chemical approximation. The formula (45) is only a valid approximation in the neighbourhood of random mixing, i.e. at high temperatures (Prigogine, Sarolea, and van Hove 1952); but at low temperatures it gives rise to minima in the free energy corresponding to phase separation, and these provide the appropriate approximation in this region.

4.4. Higher Order Approximations

There have been many attempts at improving the Bethe and quasi-chemical approximations. The most obvious method of extending the Bethe approximation is to take rigorous account of an additional shell of atoms, and to take account of the interaction of this outer shell with the remaining atoms of the lattice by the use of a mean field. In principle the approximation could then be further extended by steadily increasing the number of atoms which are treated rigorously; in practice the calculations rapidly become cumbersome, and the approximation has not been pursued beyond the second stage.

Using the combinatorial approach described at the end of the last section the quasi-chemical approximation was similarly extended by a number of writers (Yang 1945, Li 1949, Hill 1950, Guggenheim and McGlashan 1951). However, comparison with the results of known exact solutions in two dimensions (§3) indicates that the improvement proceeds rather slowly.

We have therefore preferred to present the approach of Kikuchi (1951) since this leads most simply to the maximum improvement: many other approximations will then be seen to arise as particular examples of this approach. We shall briefly survey other 'closed form' approximations in §4.4.3, and analyse in more detail the nature of the various approximations in §4.6.

4.4.1. The method of Kikuchi. Combinatorial factor

Kikuchi (1951) considered the process of constructing an ensemble of L assemblies, one unit being added to each assembly at the same time. The ratio of positive and negative spins is kept fixed in the ensemble, as are certain other ratios such as those of different types of bond, or of configurations of a square, and a direct attempt is made to calculate the number of possible complexions of the ensemble subject to these restrictions, and hence the entropy per added unit of the assembly. The method will be understood more precisely on reference to table 1:

so that one degree of freedom arises from this configuration. The next configuration is a bond shown in (b); the third column records β_i the number of equivalent configurations of a given type. Now the following relations hold

$$\left. \begin{aligned} y_1 + y_2 &= x_1, \\ y_2 + y_3 &= x_2, \end{aligned} \right\} \dots \dots \dots (47)$$

so that this configuration introduces one additional degree of freedom. The next configuration which we shall consider is a square shown in (c); the connecting relations are now

$$\left. \begin{aligned} z_1 + 2z_2 + z_3 &= y_1, \\ z_2 + z_3 + z_4 + z_5 &= y_2, \\ z_3 + 2z_5 + z_6 &= y_3, \end{aligned} \right\} \dots \dots \dots (48)$$

so that this configuration introduces three additional degrees of freedom.

If we now confine our attention to (a) and add a new unit to a lattice keeping the x_i constant, the number of possible complexions is

$$\frac{L!}{(x_1 L)!(x_2 L)!} = \frac{L!}{X_L}, \quad \dots \dots \dots (49)$$

where $X_L = \prod_{i=1}^2 (x_i L)!$.

The entropy per unit is obtained by taking the logarithm of (49) for large L , and dividing by L , and is hence

$$S(x_i) = k(-x_1 \ln x_1 - x_2 \ln x_2).$$

The internal energy must be written as a function of the x_i , and hence correspondingly the free energy; minimizing this with respect to the free variable, we obtain the equilibrium distribution of the x_i , and hence all thermodynamic properties can be deduced. This corresponds exactly to the mean field approximation. The next stage introduces y_i and configurations (b) and attempts to calculate $S(x_i, y_i)$; minimization of the free energy with respect to the free variables gives the Bethe approximation. The third stage introduces z_i and configurations (c) and attempts to calculate $S(x_i, y_i, z_i)$; minimization of the free energy now leads to an improved approximation. By taking larger elementary figures the method can clearly be extended.

We shall first consider the calculation of $S(x_i, y_i)$ for a linear chain as illustrated in fig. 4. At any stage in the construction of the ensemble $x_1 L$ of the last units added are (+) spins, and $x_2 L$ are (-) spins. Among the $x_1 L$ units we can select $y_1 L$ at random and attach (+) spins to them, giving $y_1 L$ (+ +) bonds; to the remaining $y_2 L$ of the $x_1 L$ units we attach (-) bonds giving $y_2 L$ (+ -) bonds. The combinatorial factor associated with this procedure will be $(x_1 L)!/(y_1 L)!(y_2 L)!$. We now attach (+) and (-) spins in an analogous manner to the $x_2 L$ (-) spins with combinatorial

factor $(x_3L)!(y_2L)!(y_3L)!$. Hence the total combinatorial factor arising from the addition of a new unit is

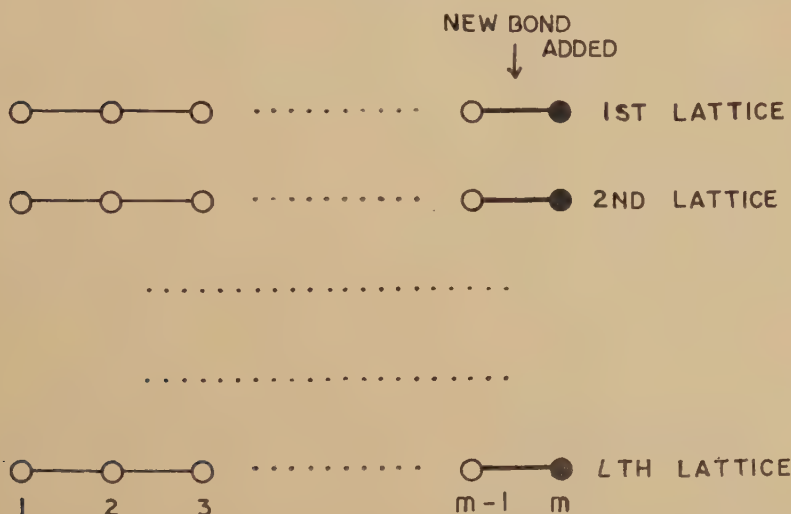
$$\frac{(x_1L)!(x_2L)!}{(y_1L)!(y_2L)!^2(y_3L)!} = \frac{X_L}{Y_L}, \quad \dots \quad (50)$$

where $Y_L = \prod_{i=1}^3 (y_iL)^{\beta_i}$. The corresponding entropy is

$$S(x_i, y_i) = k \left[\sum_{i=1}^2 x_i \ln x_i - \sum_{i=1}^3 \beta_i y_i \ln y_i \right]. \quad \dots \quad (51)$$

The relations (47) will ensure that of the new units added x_1L are (+) spins and x_2L (-) spins. For the one-dimensional chain there is no approximation in the procedure and formula (51) is exact.

Fig. 4



Building up an ensemble of linear lattices. The last bond is added in such a manner as to maintain a given ratio of + to - spins in the ensemble.

We now attempt to apply the same procedure to the two-dimensional quadratic lattice as illustrated in fig. 5(a). We wish to find the combinatorial factor arising from the addition of a unit A, when units B and C have the distribution x_i , and the bonds AB and AC have the distribution y_i in the ensemble. Let us first add bonds BA', CA'' (fig. 5(b)) as in the one-dimensional case, the combinatorial factor for this procedure being then $(X_L/Y_L)^2$. Both A' and A'' will have the distribution x_i in the ensemble; however, to add the unit A correctly we must examine the detailed distribution of (+) and (-) spins in the ensemble for every pair of configurations A' and A'' and only count those for which these detailed distributions are identical. Hence the expression $(X_L/Y_L)^2$ must be multiplied by a correcting factor to obtain

To improve the approximation we build up the lattice using a square as the basic elementary figure. We introduce the angle configurations in table 1 (*d*) to help in the construction of the lattice, but they do not enter into the final result. The unit A is to be added so that the square ABDC has distribution z_i , and the angles BDC, ACE have distribution w_i in the ensemble. As before we construct the configurations BDCA', ECA'' with appropriate distributions (fig. 5 (*c*)) having combinatorial factors

$$W_L/Z_L, Y_L/W_L \text{ respectively } \left(Z_L = \prod_{i=1}^6 (z_i L)!^{\gamma_i}, W_L = \prod_{i=1}^6 (w_i L)!^{\delta_i} \right).$$

To obtain the correct combinatorial factor we must now pair together complexions for which the detailed distributions in the bonds CA', CA'' are identical. Again we cannot correct exactly, but we assume as an approximation that the bonds CA', CA'' are uncorrelated; we must therefore divide the total number of complexions obtained by independent pairing by the number of possible complexions of a bond CA', C having given distribution x_i , and we thus obtain for the combinatorial factor

$$\frac{W_L}{Z_L} \cdot \frac{Y_L}{W_L} \div \frac{X_L}{Y_L} = Y_L^2 / (X_L Z_L). \quad . \quad . \quad . \quad (55)$$

The entropy in this approximation is then given by

$$S(x_i, y_i, z_i) = k \left[- \sum_{i=1}^2 x_i \ln x_i + 2 \sum_{i=1}^3 \beta_i y_i \ln y_i - \sum_{i=1}^6 \gamma_i z_i \ln z_i \right]. \quad (56)$$

Kikuchi (1951) applied a similar method to the simple cubic lattice, obtaining for the combinatorial factor $Y_L^9 L! / (Z_L^3 X_L^7)$, and for the entropy

$$S(x_i, y_i, z_i) = k \left[- 7 \sum_{i=1}^2 x_i \ln x_i + 9 \sum_{i=1}^3 \beta_i y_i \ln y_i - 3 \sum_{i=1}^6 \gamma_i z_i \ln z_i \right]. \quad (57)$$

Similarly he obtained improved approximations for the triangular and face-centred cubic lattices.

However, the above argument is not easy to follow in the more complex cases, and in a subsequent paper, Kurata *et al.* (1953) suggested an alternative development of the approximation which enables the appropriate combinatorial factor to be written down more readily. This is briefly illustrated in fig. 6; the elementary figures from which the lattice is constructed are all drawn in separately, and the factor necessary to select only configurations in which all spins at a given lattice point are identical is estimated. It is found that, for example, if the lattice consists of tN squares, sN bonds and rN points the combinatorial factor is

$$(L!)^{t-s+r} Y_L^{4t-s} / X_L^{4t-2s+r} Z_L^t, \quad . \quad . \quad . \quad (58)$$

and this will be found to include (55) and (57) ($t=1, s=2, r=1$ and $t=3, s=3, r=1$).

A systematic analysis of the Kikuchi method together with a technique for determining the combinatorial factor in the most general case is provided in a comprehensive series of papers by Hijmans and de Boer (1955, 1956).

4.4.2. *Evaluation of thermodynamic properties*

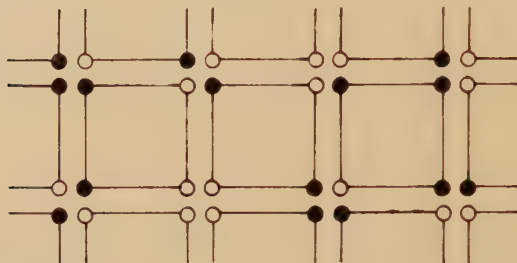
The internal energy per spin of any configuration is given by

$$E^I = -mH(x_2 - x_1) - \frac{1}{2}qJ(y_1 + y_3 - 2y_2) = mH(x_1 - x_2) - \frac{1}{2}qJ + 2qJy_2 \quad (59)$$

and the equilibrium values of x_i , y_i , z_i are determined by minimizing the free energy $F^I = (E^I - TS)$ with respect to the free parameters. We have noted that relations (46) (47) and (48) leave five degrees of freedom. It is useful to choose free parameters which have a direct physical significance; thus

$$\left. \begin{aligned} \xi_1 &\equiv x_1 - x_2, \\ \xi_2 &\equiv z_2 - z_5, \end{aligned} \right\} \quad \cdot \cdot \cdot \cdot \cdot \cdot \quad (60)$$

Fig. 6



From the above assembly only configurations in which all spins at a lattice point are identical must be selected.

have the significance of long-range order parameters and will be zero for a disordered state in the absence of a magnetic field. For the other free parameters we choose y_2 , z_3 and z_4 ; the remaining dependent variables can then readily be expressed as linear combinations of these e.g.

$$2z_1 = 1 + \xi_1 - 2\xi_2 - 4y_2 + 2z_4, \quad \cdot \cdot \cdot \cdot \cdot \quad (61)$$

Taking as an example the second approximation for the simple cubic lattice, (57), we obtain:

$$\left. \begin{aligned} \partial F^I / \partial \xi_1 &= 0, & (x_1/x_2)^7 (y_3/y_1)^9 (z_1/z_6)^3 &= \mu, & \text{(i)} \\ \partial F^I / \partial y_2 &= 0, & [y_2^2/(y_1 y_3)]^3 [z_1 z_6/(z_2 z_5)]^2 &= z^{-2}, & \text{(ii)} \\ \partial F^I / \partial z_3 &= 0, & z_3^2 &= z_2 z_5, & \text{(iii)} \\ \partial F^I / \partial z_4 &= 0, & z_2^2 z_5^2 &= z_4^2 z_1 z_6, & \text{(iv)} \\ \partial F^I / \partial \xi_2 &= 0, & (z_2/z_5)^2 &= z_1/z_6 & \text{(v)}. \end{aligned} \right\} \quad \cdot \quad (62)$$

These equations can in general be reduced to a single algebraic equation in one variable, and the thermodynamic functions can be derived from (57) and (59) by numerical computation.

In the absence of a magnetic field ($\mu = 1$) we look for critical phenomena corresponding to the appearance of long-range order. The disordered state

at sufficiently high temperatures will be characterized by $\xi_1 = \xi_2 = 0$, and eqns. (i) and (v) above become identities. The remaining equations simplify considerably, and an explicit solution is possible in terms of a single parameter ϕ as follows:

$$\left. \begin{aligned} z^{-1} &= [(3\phi + 1)/(\phi + 3)]^3/\phi, \\ z_4 &= [2(\phi^2 + 6\phi + 1)]^{-1}, \\ z_3 &= \phi z_4, \\ y_2 &= (3\phi + 1)z_4. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (63)$$

(For details of the calculations see Kikuchi (1951).)

The ordered phase is more complicated since it depends on five parameters, and the detailed properties must be determined by numerical computation. However the critical point (and hence critical values) can be determined by examining eqns. (62) for the onset of non-zero solutions for ξ_1 and ξ_2 . By analogy with the conclusions of the Bethe approximation (31) we may assume that just below the Curie point the values of $\delta\xi_1$ and $\delta\xi_2$ will be an order of magnitude larger than the changes in any of the other parameters. Hence if we consider a small change in equations (i) and (v) taking account only of $\delta\xi_1$ and $\delta\xi_2$, and eliminate $\delta\xi_1$, $\delta\xi_2$ we shall obtain an additional relation to (63) from which the Curie point can be determined. We find that (putting $\xi_1 = \xi_2 = 0$ after differentiating)

$$\frac{\delta\xi_1}{\delta\xi_2} = \frac{6}{z_1} \left/ \left\{ 14 - \frac{9}{y_1} + \frac{3}{z_1} \right\} \right. = \left\{ \frac{2}{z_1} + \frac{2}{z_2} \right\} \left/ \frac{1}{z_1} \right. . \quad . \quad . \quad (64)$$

From (63) and (64) we deduce that

$$\phi_c = 3, \quad kT_c/J = 4.6097. \quad . \quad . \quad . \quad . \quad . \quad (65)$$

The specific heats on the high and low temperature sides of T_c are given by

$$\left. \begin{aligned} c_+/k &= 0.389, \\ c_-/k &= 2.902. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (66)$$

We shall defer until § 4.6, § 4.7 a detailed discussion of the physical conclusions arising from the application of the Kikuchi method to various lattices.

It is perhaps worth observing that by giving some parameters fixed values corresponding to a high temperature and varying the others, some estimate can be obtained from this approximation of non-equilibrium effects such as 'frozen in' order.

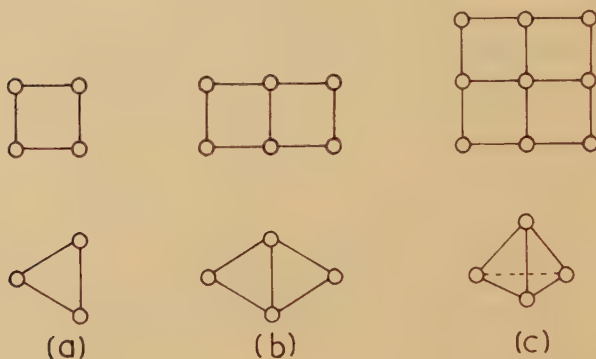
4.4.3. Other approximations

The first approximation which registered a marked improvement over the Bethe approximation was the variation method introduced by Kramers and Wannier in 1941. We have seen in § 3.2.2. that the partition function for the Ising model is determined by the largest eigenvalue of a symmetric matrix. By assuming an eigenvector ξ dependent on a number of parameters and minimizing $\xi' V \xi / (\xi' \xi)$ with respect to these parameters a

useful estimate can be obtained of the largest eigenvalue. Kramers and Wannier applied this method to the quadratic lattice and obtained results which were exactly reproduced by Kikuchi (1951) from eqn. (56). The method was extended to the simple cubic lattice by ter Haar and Martin (1950), but the detailed calculations for three-dimensional models are considerably more complex. The accuracy of the results in this case seems comparable with that of Kikuchi. (The technique of comparing various approximations will be discussed in §4.6.)

In their 1953 paper Kurata *et al.* considered the possibility of using the Kikuchi method with different types of basic elementary figure. They pointed out that the choice of a larger basic figure could result in little or no improvement of a preceding approximation. In fact they suggested that in order to improve an approximation it is necessary to adopt a basic figure

Fig. 7



Examples of open and closed clusters. (a) Represents an elementary figure, (b) are *open* and, (c) are *closed* with respect to (a).

which is 'closed' with respect to the basic figure in the preceding approximation. The terms 'open' and 'closed' are defined as follows. If the fraction of occurrences of a cluster B (table 1) can be (cannot be) derived rigorously from those of its sub-cluster A, B is said to be open (closed) with respect to A. For example, in fig. 7 (b) are *open* and (c) *closed* with respect to the corresponding (a). Subsequently Hijmans and de Boer (1955) showed that this statement is not completely valid, and that a more careful analysis is required; it can nevertheless serve as a useful guide. The approximations of Yang (1945), Li (1949), Hill (1950), Guggenheim and McGlashan (1951) and Fosdick and James (1953) correspond to the choice of a particular elementary figure, and are intermediate between the first and second order approximations of Kikuchi.

Prigogine, *et al.* (1952) suggested an ingenious improvement of the quasi-chemical combinatorial factor (45) based on a comparison with the known exact factor for the Onsager solution. However, they did not undertake any detailed thermodynamic calculations other than the evaluation of the

Curie point (which resulted in a substantial improvement) since such calculations would seem to be quite involved. It is difficult to assess the precise status of this approximation.

It is similarly difficult to draw definite conclusions regarding the approximation of Cowley (1950). Following Zernike (1940), Cowley attempted directly to calculate the order between different pairs of lattice sites, but he assumed that the order parameters corresponding to pairs of sites at different distances are independent. The resulting specific heat singularity is infinite of order $(T_c - T)^{-1/2}$, but the estimate of the Curie temperature is no better than the mean-field approximation. The method of Yvon to be described in § 4.5.2. seems to provide an exact description of this approach with no arbitrary assumptions.

The 'constant coupling' approximation was introduced by Kasteleijn and van Kranendonk in 1956. Its most important achievement was the provision of a 'quasi-chemical' approximation for the Heisenberg model. However, the authors showed that the same technique could be applied to the Ising model.

Recently Levitas and Lax (1958) introduced a technique which is a combination of the 'spherical model' and the Bethe approximation (the 'spherical model' replaces the Ising interaction by an alternative interaction for which the partition function can be calculated exactly; see Berlin and Kac 1952). In two dimensions the results obtained are appreciably wrong; but for the simple cubic lattice in three dimensions a remarkably accurate estimate is obtained for the critical temperature. However, the precise status of this approximation is again difficult to establish.

4.5. *Methods Based on Series Expansions*

We have seen in § 3.6 how exact expansions for the partition function can be formulated at high and low temperatures. The derivation of substantial numbers of terms of such expansions requires a specialized technique which is described in detail in § 5. We shall quote the results of such derivations, and discuss how they can best be used to provide information regarding the physical properties of the model.

Two alternative procedures have been employed. A particular selection of terms which can readily be evaluated has been summed to provide closed form approximations similar to those discussed previously; however, the nature of the approximation and of the terms ignored is known precisely at each stage. This is the basis of the methods described in §§ 4.5.1, 4.5.2. Alternatively, direct use can be made of the known terms of a series expansion to assess its asymptotic behaviour, and hence estimate its sum. This approach is described in §§ 4.5.3, 4.5.4.

In the first method extensive use is made of the Mayer theory of cluster integral expansions (Mayer and Mayer 1940, Chs. 13, 14). The theory was first applied to the Ising problem by Fuchs (1942), but a substantial amplification was made by Rushbrooke and Scoins (1955). A somewhat analogous approach to the problem was initiated independently by Yvon in 1945.

We shall quote here for convenience the main formulae needed from the Mayer theory. This theory applies to a gas in which the interaction energy, $V(r_{ij})$ between any pair of molecules i, j is a function of their distance apart, r_{ij} , and can be taken as zero beyond a certain range. Introducing the functions

$$f_{ij} = f(r_{ij}) = \exp [-V(r_{ij})/kT] - 1, \quad . \quad . \quad . \quad . \quad (67)$$

the grand partition function can be expanded in the form

$$\frac{1}{V} \ln \Xi = \sum_{t \geq 1} \lambda^t b_t, \quad . \quad . \quad . \quad . \quad (68)$$

where b_t are cluster integrals defined by

$$V b_t = \frac{1}{t!} \sum \int \dots \int_{(t)} f_{ij} f_{jk} \dots f_{kl} d\tau_1 \dots d\tau_t. \quad . \quad . \quad . \quad (69)$$

Each cluster integral corresponds to a different connected graph among the t labelled points, and the sum must be taken over all possible graphs. λ is the absolute activity, and is determined in terms of the density ρ by

$$\rho = \lambda \frac{\partial}{\partial \lambda} \left(\frac{1}{V} \ln \Xi \right) = \sum_{t \geq 1} t \lambda^t b_t. \quad . \quad . \quad . \quad . \quad (70)$$

It is one of the most remarkable properties of the Mayer theory that the elimination of λ between (68) and (70) leads to the formula

$$\frac{1}{V} \ln \Xi = \rho \left(1 - \sum_{u \geq 1} \frac{u}{u+1} \beta_u \rho^u \right), \quad . \quad . \quad . \quad . \quad (71)$$

where the β_u are 'irreducible' cluster integrals. These are defined similarly to (69) by

$$\beta_u = \frac{1}{u!} \sum^* \int \dots \int_{(u)} f_{ij} f_{jk} \dots f_{kl} d\tau_2 \dots d\tau_{u+1}, \quad . \quad . \quad (72)$$

but the sum in (72) is taken over graphs among $(u+1)$ labelled points which are multiply connected (when $u > 1$), i.e. in which any two points of the graph are connected by at least two paths having no common point other than their ends. The elimination of all but multiply connected graphs is a substantial simplification.

We shall first describe the approach of Fuchs and Rushbrooke and Scoins because formulae are derived for the regular assembly problem which directly parallel eqns. (68) to (72).

4.5.1. *The method of Rushbrooke and Scoins*

In order to simplify the analogy between the Mayer theory and regular assemblies it is better to consider the problem in which 1 units are molecules and 2 units are vacancies, so that in the notation of § 2.1 $\epsilon_{12} = \epsilon_{22} = 0$, $\epsilon = -\frac{1}{2} \epsilon_{11}$. From the general discussion in § 2 the function

$$\Lambda_N(\mu, z) = \sum_{N_1, N_{12}} g(N; N_1, N_{12}) \mu^{N_1} z^{N_{12}} \quad . \quad . \quad . \quad (73)$$

can be regarded as a configurational partition function from which all thermodynamic properties of the Ising model and other corresponding physical assemblies can be derived.

To introduce the Mayer formalism for systems restricted to certain lattice sites, we observe that interaction energies arise only for certain discrete values of the distance r_{ij} . In fact, $V(r_{ij})$ now has the three possible values, $+\infty$ (when $r_{ij}=0$), ϵ_{11} (when i and j occupy neighbouring sites), and 0 (otherwise). Hence instead of (67) we shall now expect

$$f_{ij} = \left\{ \begin{array}{ll} -1 & \text{if the two systems are on the same lattice point,} \\ z^{-2} - 1 & \text{if the two systems are on adjacent lattice points,} \\ 0 & \text{otherwise,} \end{array} \right\} \quad (74)$$

where $z = \exp [\epsilon_{11}/2kT]$ as in § 2 (4).

Making the substitution

$$z^{-2} = 1 + f \quad (75)$$

in (73), and using the relation [§ 2 (2)] $2N_{11} + N_{12} = qN_1$, we obtain

$$\Lambda_N(\mu, z) = \sum_{N_1, N_{11}} g(N; N_1, N_{12}) (\mu z^q)^{N_1} (1+f)^{N_{11}} \quad (76)$$

To complete the analogy with the Mayer theory we must now label the N_1 systems (thus introducing a factor $1/N_1!$) and rewrite (76) in the form

$$\Lambda_N(\mu, z) = \sum_{N_1} \frac{(\mu z^q)^{N_1}}{N_1!} \mathbf{S} \prod_{i>j} (1+f_{ij}) \quad (77)$$

where the f_{ij} are given by (74), \mathbf{S} denotes summation over discrete values instead of integration, and the product is taken over all pairs of molecules. The Mayer formalism can be applied exactly to (77) (Mayer and Mayer 1940, sections 12 b and 13 a), and we obtain formulae equivalent to (68) and (70)

$$\ln \Lambda(\mu, z) = \sum_{t \geq 1} \lambda^t b_t(z), \quad (\lambda = \mu z^q) \quad (78)$$

$$\alpha_1 = \sum_{t \geq 1} t \lambda^t b_t(z), \quad (79)$$

where the $b_t(z)$ are now cluster sums defined by

$$N b_t(z) = \frac{1}{t!} \sum_{(t)} \mathbf{S} f_{ij} f_{jk} \dots f_{kl} \quad (80)$$

the connected graphs being defined as in (69). Comparing (78) with § 3 (146) or § 5 (115) we see that

$$z^{tq} b_t(z) = g_t(z). \quad (81)$$

As a simple application of (80) we shall evaluate the first three cluster sums corresponding to the graphs \cdot , $-$, \triangle , \wedge . For each type of graph the sum (80) must be evaluated for all possible configurations of the systems on the lattice, remembering to take account of contributions which occur when two or more systems occupy the same lattice point.

(i) \cdot clearly gives $b_1(z) = 1$.

(ii) $1-2$ When 1 and 2 are nearest neighbour lattice points the graph gives a contribution f . There are $Nq/2$ such links in the lattice, and taking account of interchange of 1 and 2 we obtain a contribution to $b_2(z)$ of $qf/2$.

When 1 and 2 are the same lattice point the contribution is $-\frac{1}{2}$. Hence $b_2(z) = (qf - 1)/2$.

(iii) ${}_2\Delta_3$ When all the vertices are nearest neighbours the contribution is $p_3 f^3$ where Np_3 is the number of triangles in the lattice (§ 5.1.1); when two of the vertices coincide we obtain a contribution $-qf^2/2$; when all three coincide the contribution is $-\frac{1}{6}$. ${}_2\Delta_3$ When 1-2 and 2-3 correspond to nearest neighbour links the contribution is

$$\frac{q(q-1)}{2} f^2;$$

when 2 and 3 coincide the contribution is $(q/2)f^2$; when 1 and 2 coincide the contribution is $-qf$; when all three coincide the contribution is $\frac{1}{2}$. Hence

$$b_3(z) = p_3 f^3 + \frac{q(q-1)}{2} f^2 - qf + \frac{1}{3}.$$

The problem of deriving higher terms depends on the enumeration of different types of configuration on lattices, and is discussed in § 5.4.1 (see also Katsura 1958 and Temperley 1959).

Continuing the analogy with the Mayer theory Rushbrooke and Scoins used (78) and (79) to eliminate λ and hence express $\ln \Lambda$ as a power series in α_1 analogous to (71),

$$\ln \Lambda(\alpha_1, z) = \alpha_1 \left(1 - \sum_{u \geq 1} \frac{u}{u+1} \beta_u \alpha_1^u \right). \quad . \quad . \quad . \quad . \quad (82)$$

β_u are now irreducible cluster sums

$$\beta_u = \frac{1}{u!} \sum_{(u)}^* \mathbf{S} f_{ij} f_{jk} \dots f_{kl}, \quad . \quad . \quad . \quad . \quad . \quad (83)$$

taken over multiply connected paths among the $(u+1)$ points. β_u is evaluated by keeping system 1 fixed and allowing systems 2, 3, ..., $(u+1)$ to take up all possible positions on the lattice. Rushbrooke and Scoins then proved that, despite the multiple occupation of lattice points, non-zero contributions are obtained only from configurations in which the *lattice points* are multiply connected. $\beta_1(z)$ and $\beta_2(z)$ are thus derived from the graphs $-, \Delta$ respectively, and proceeding as for $b_i(z)$ we find that

$$\left. \begin{aligned} \beta_1(z) &= qf - 1 \\ \beta_2(z) &= 3p_3 f^3 - 3qf^2/2 - 1/2. \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (84)$$

It will be noted that each $\beta_u(z)$ can be divided into various contributory terms; pure numbers arise from configurations representing multiple occupation of single lattice points; terms linear in q arise from configurations representing occupation (single or multiple) of two nearest-neighbour lattice points; terms linear in p_3 arise from configurations representing occupation (single or multiple) of three nearest-neighbour lattice points forming a triangle; and so on. Thus we may write

$$\beta_u = \beta_u^{(0)} + \frac{q}{2} \beta_u^{(1)} + p_3 \beta_u^{(3)} + p_4 \beta_u^{(4)} + p_{5a} \beta_u^{(5a)} + \dots \quad . \quad . \quad (85)$$

where Np_3 , Np_4 , Np_{5a} represent the numbers of various types of multiply-connected configuration on the lattice (§ 5.1.1). Hence substituting in (82) and summing each particular class, we may write

$$\ln \Lambda(\alpha_1, z) = H_1(\alpha_1, z) + \frac{q}{2} H_2(\alpha_1, z) + p_3 H_3(\alpha_1, z) \\ + p_4 H_4(\alpha_1, z) + p_{5a} H_{5a}(\alpha_1, z) + \dots \quad (86)$$

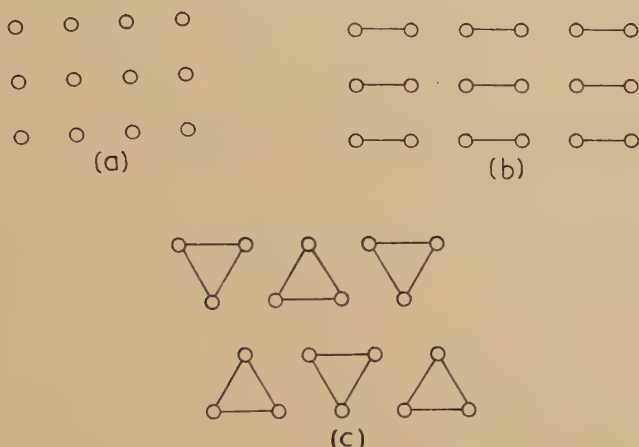
To determine $H_1(\alpha_1, z)$ we may consider a pseudo-lattice of N isolated systems (fig. 8a) for which $q=0$, $p_3=0$, $p_4=0 \dots$ but for which all the conditions of the Mayer theory apply. For such a pseudo-lattice $\Lambda(\mu, z) = 1 + \mu$; hence $\alpha_1 = \mu/(1 + \mu)$, $\mu = \alpha_1/(1 - \alpha_1)$, and

$$H_1(\alpha_1, z) = -\ln(1 - \alpha_1). \quad (87)$$

Using (82) and (85) we deduce that

$$\beta_u^{(0)} = -1/u. \quad (88)$$

Fig. 8



Examples of pseudo-lattices to which the Mayer theory is applicable. (a) Isolated spins. (b) Isolated pairs of spins. (c) Isolated triangles of spins.

Similarly to determine $H_2(\alpha_1, z)$ we consider a pseudo-lattice made up of $N/2$ isolated pairs of points (fig. 8b) for which $q=1$, $p_3=0$, $p_4=0$.

For this pseudo-lattice

$$\left. \begin{aligned} \ln \Lambda(\mu, z) &= \frac{1}{2} \ln(1 + 2\mu z + \mu^2), \\ \alpha_1 &= \frac{\mu(\mu + z)}{1 + 2\mu z + \mu^2}, \end{aligned} \right\} \quad (89)$$

and we deduce that

$$H_2(\alpha_1, z) = \ln[(1 - \alpha_1) + \frac{1}{2} z^2 (2\alpha_1 - 1 + \zeta)]. \quad (90) \\ (\zeta = \sqrt{[1 + 4\alpha_1(1 - \alpha_1)f]})$$

Again by expanding (90) as a power series in α_1 we can calculate $\beta_u^{(2)}$.

We can determine $H_l(\alpha_1, z)$ for any simple l -sided polygon by using a pseudo-lattice made up of N/l isolated polygons. For such a pseudo-lattice $q=2$, $p_l=1/l$ and all other p_{lx} are zero; also for this assembly (§ 3.2.1)

$$\left. \begin{aligned} \ln \Lambda(\mu, z) &= \frac{1}{l} \ln [\Lambda_1^l + \Lambda_2^l], \\ \Lambda_1 &= \frac{1}{2} \{1 + \mu \pm \sqrt{[(1-\mu)^2 + 4\mu z^2]}\}, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (91)$$

and hence $H_l(\alpha_1, z)$ and $\beta_u^{(0)}$ can be determined. This powerful technique of rearranging the terms of (82) in the form (86) and using finite clusters to find the initial terms of the latter series seems first to have been used by Yvon (1945).

Rushbrooke and Scoins pointed out that stopping the series (86) after the first term corresponds to the approximation of random mixing; inclusion of the second term corresponds to the quasi-chemical approximation; and the addition of further terms gives rise to improved approximations. They calculated the critical points for various lattices using such improved approximations, and found the results in general better than the approximations of Yang-Li-Hill and Guggenheim and McGlashan (§ 4.4.3) but not as good as the approximation of Kikuchi (§§ 4.4.1, 4.4.2). In fact the method as outlined so far can only take account of homogeneous configurations (§ 5.2.9) in which all vertices have the same coordination number; a great improvement would probably be registered by calculating terms in (86) corresponding to non-homogeneous configurations (e.g. $H_{5a}(\alpha_1, z)$), but this would first require a generalization of the theory to apply to non-homogeneous lattices.

4.5.2. The method of Yvon†

It is unfortunate that Yvon's papers (1945, 1948) describing his method were published in a rather obscure journal. His approach is particularly comprehensive, and has not received the attention which it deserves. The extension and application of the method to a variety of physical problems is due to Fournet (1952, 1953, 1957).

Yvon starts from his own development of the cluster integral theory enunciated in a classical memoir on density fluctuations (1937). Considering an assembly of N interacting molecules in an external field $U(r)$, and using the notation of the previous section for f_{ij} , the configurational partition function is given by

$$Z_N = \int \dots \int \prod_{i=1}^N f_i \prod_{\substack{i,j=1 \\ (i < j)}}^N (1 + f_{ij}) \prod_{i=1}^N d\tau_i, \quad . \quad . \quad . \quad . \quad (92)$$

where

$$f_i = \exp [-U(r_i)kT].$$

† For the cluster integral development in this section it is convenient to use the numbers 1, 2 to refer to different systems of the assembly, and not as previously to different states of individual systems.

For the density at a given point 1 we have similarly

$$\rho_1 Z_N = \int \dots \int_{(N-1)} \prod_{i=1}^N f_i \prod_{\substack{i,j=1 \\ (i < j)}}^N (1 + f_{ij}) \prod_{i=2}^N d\tau_i \quad . \quad . \quad . \quad (93)$$

The product $\prod_{\substack{i,j=1 \\ (i < j)}}^N (1 + f_{ij})$ will be denoted by $A_{12\dots N}$. This can be expanded in the usual manner in terms of clusters of various order; a grouping can then be undertaken with special reference to the particular system 1. The first group consists of all clusters not involving system 1, and these sum to $A_{23\dots N}$. The second group consists of all clusters in which system 1 is part of a 2-cluster (e.g. $f_{12}f_{34}f_{45}f_{78}$ or $f_{13}f_{24}f_{45}f_{52}$); the terms involving f_{12} sum to $f_{12} A_{345\dots N}$ and there will be $(N-1)$ terms of the same kind which we denote by $\sum_{(2)} f_{12} A_{345\dots N}$. The third group consists of all clusters in which system 1 is part of a 3-cluster; as in the Mayer development it is convenient to label the systems other than 1 and divide by $(t-1)!$ for a t -cluster; this group may then be written

$$\sum_{(2,3)} (\tfrac{1}{2}f_{12}f_{13} + f_{12}f_{23} + \tfrac{1}{2}f_{12}f_{13}f_{23}) A_{45\dots N},$$

the sum consisting of $(N-1)(N-2)$ terms. Thus we may write

$$A_{12\dots N} = A_{23\dots N} + \sum_{(2)} f_{12} A_{345\dots N} + \sum_{(2,3)} (\tfrac{1}{2}f_{12}f_{13} + f_{12}f_{23} + \tfrac{1}{2}f_{12}f_{13}f_{23}) A_{45\dots N} + \dots \quad (94)$$

Substituting (94) in (93), and using (92), we find that

$$\begin{aligned} \rho_1 Z_N = & j_1 [Z_{N-1} + Z_{N-2} (1 - 1/N) \int f_{12} j_2 d\tau_2 \\ & + Z_{N-3} (1 - 1/N) (1 - 2/N) \int \int (\tfrac{1}{2}f_{12}f_{13} + f_{12}f_{23} + \tfrac{1}{2}f_{12}f_{13}f_{23}) \\ & + j_2 j_3 d\tau_2 d\tau_3 + \dots] \quad . \quad . \quad . \quad (95) \end{aligned}$$

where

$$j_i = N f_i / \int f_i d\tau_i.$$

In the limiting case of large N , assuming $Z_N \sim Z^N$, and neglecting terms of order $1/N$, (95) can be written

$$\rho_1 = q_1 \left[1 + \int f_{12} q_2 d\tau_2 + \int \int (\tfrac{1}{2}f_{12}f_{13} + f_{12}f_{23} + \tfrac{1}{2}f_{12}f_{13}f_{23}) q_2 q_3 d\tau_2 d\tau_3 + \dots \right] \quad . \quad . \quad . \quad (96)$$

where

$$q_1 = j_1 / Z.$$

Considering as an example the equilibrium distribution of a fluid under gravity Yvon concluded that the series (96) was very slowly convergent. However, treating the series as an integral equation for the determination of an unknown function $q_1(x, y, z)$, the solution could be obtained by inversion as follows:—

$$q_1 = \rho_1 \left[1 - \int f_{12} p_2 d\tau_2 - \int \int (-\tfrac{1}{2}f_{12}f_{13} + \tfrac{1}{2}f_{12}f_{13}f_{23}) \rho_2 \rho_3 d\tau_2 d\tau_3 - \dots \right] \quad . \quad . \quad . \quad (97)$$

Finally, taking logarithms in (97) a series is obtained, as in the Mayer theory, in which only multiply connected clusters enter :

$$\ln q_1 = \ln \rho_1 - \int f_{12} \rho_2 d\tau_2 - \int \int \frac{1}{2} f_{12} f_{13} f_{23} \rho_2 \rho_3 d\tau_2 d\tau_3 + \dots \quad (98)$$

$$= C - U_1/kT$$

Here $C = \ln [N/Z (\int f_i d\tau_i)]$ is a function of temperature and volume alone, and independent of position. In the series (98) the general term is the sum of all multiply connected clusters of order t divided by $(t-1)!$ remembering that the system 1 is specialized and that the remaining $(t-1)$ can be permuted. For example the fourth term can be written symbolically

$$- \left\{ \frac{1}{2} \begin{array}{c} 1 \quad 3 \\ \text{---} \text{---} \\ | \quad | \\ 2 \quad 4 \end{array} + \frac{1}{2} \begin{array}{c} 1 \quad 3 \\ \text{---} \text{---} \\ | \quad \diagdown \\ 2 \quad 4 \end{array} + \frac{1}{2} \begin{array}{c} 1 \quad 3 \\ \text{---} \text{---} \\ \diagup \quad | \\ 2 \quad 4 \end{array} + \frac{1}{6} \begin{array}{c} 1 \quad 3 \\ \text{---} \text{---} \\ \diagup \quad \diagdown \\ 2 \quad 4 \end{array} \right\} \quad (99)$$

Considering again the example of a fluid under gravity Yvon concluded that the series (98) is rapidly convergent.

The same procedure is now applied to the correlation ρ_{12} between the systems 1 and 2 using the equation

$$\rho_{12} Z_N = \int \dots \int_{(N-2)} \prod_{i=1}^N f_i \prod_{\substack{i,j=1 \\ (i < j)}}^N (1 + f_{ij}) \prod_{i=3}^N d\tau_i \quad (100)$$

In all expansions based on (100) systems 1 and 2 are given special attention, and instead of (94) the appropriate expansion is

$$A_{123\dots N} = A_{34\dots N} + \sum_{(3)} (f_{13} + f_{23} + f_{13}f_{23}) A_{45\dots N} \\ + \sum_{(3,4)} (\frac{1}{2}f_{13}f_{14} + f_{13}f_{34} + \dots) A_{56\dots N} + \dots \quad (101)$$

Substituting in (100) we obtain, in the limit of large N ,

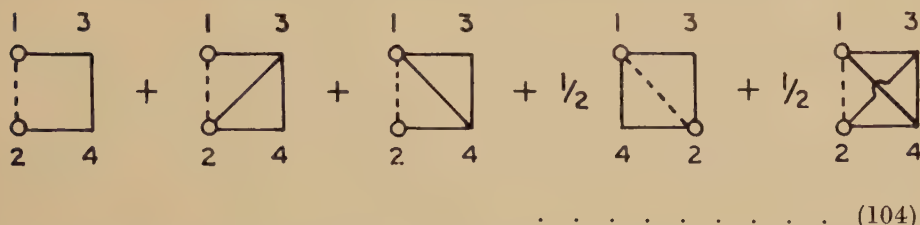
$$\rho_{12} = q_1 q_2 \exp [-V(r_{12})/kT] \left\{ 1 + \int (f_{13} + f_{23} + f_{13}f_{23}) q_3 d\tau_3 \right. \\ \left. + \int \int (\frac{1}{2}f_{13}f_{14} + f_{13}f_{34} + \dots) q_3 q_4 d\tau_3 d\tau_4 + \dots \right\} \quad (102)$$

Using (97) to eliminate the q_i , we finally derive as an analogous equation to (97)

$$\rho_{12} = \rho_1 \rho_2 \exp [-V(r_{12})/kT] \left\{ 1 + \int f_{13} f_{23} \rho_3 d\tau_3 \right. \\ \left. + \int \int (f_{13} f_{24} f_{34} + f_{13} f_{14} f_{24} f_{34} + \dots) \rho_3 \rho_4 d\tau_3 d\tau_4 + \dots \right\} \quad (103)$$

Here the general term is the sum of all multiply-connected clusters of order t (with the completion of the bond 12) divided by $(t-2)!$, remembering

that systems 1 and 2 are specialized and that the remaining $(t-2)$ can be permuted. Thus the terms involving 4-clusters can be written



$$\dots \dots \dots (104)$$

Equations (98) and (102) are the master equations in Yvon's theory. The application to crystal lattices proceeds as in the previous section, the integrals being replaced by sums. We may thus write instead of (98) and (102) for two neighbouring lattice sites a and b †:

$$\ln \alpha_a - \sum_i f_{ai} \alpha_i - \frac{1}{2} \sum_{i,j} f_{ai} f_{aj} f_{ij} \alpha_i \alpha_j - \dots = C - \frac{U_a}{kT} \quad (105)$$

$$\alpha_{ab} = \alpha_a \alpha_b (1 + f_{ab}) \left[1 + \sum_i f_{ai} f_{bi} \alpha_i + \sum_{i,j} (f_{ai} f_{bj} f_{ij} + f_{ai} f_{aj} f_{bj} f_{ij} + \dots) \alpha_i \alpha_j + \dots \right] \quad (106)$$

Here f_{ij} is defined by (74), and the sums $f_{ai}, f_{bj}, f_{ij} \dots$ for $i, j \dots k$ must be taken over all pairs of lattice points which coincide or are nearest neighbours; the detailed enumeration of the terms in (105) follows (99), and in (106) follows (104).

The terms in (105) may now be rearranged as in the previous section into groups corresponding to occupation (single or multiple) of a single lattice point, occupation (single or multiple) of two nearest-neighbour lattice points, occupation (single or multiple) of three nearest-neighbour lattice points forming a triangle, and so on. By analogy with (86) we can write for the left-hand side of (105).

$$J_1(\alpha_a; z) + \sum_b J_2(\alpha_a, \alpha_b; z) + \sum_{b,c} J_3(\alpha_a, \alpha_b, \alpha_c; z) + \sum_{b,c,d} J_4(\alpha_a, \alpha_b, \alpha_c, \alpha_d; z) + \dots, \quad (107)$$

the first sum being taken over the q nearest neighbours b of a , the second sum over the other vertices b, c of the $3p_3$ triangles passing through a , and so on. The terms $J_1(\alpha_a; z)$, $J_2(\alpha_a, \alpha_b; z)$, $J_3(\alpha_a, \alpha_b, \alpha_c; z) \dots$ can again be found explicitly by applying (105) to pseudo-lattices (fig. 8); the constant C can be eliminated by considering explicitly the first few terms of the expansion (105). We thus readily find from the pseudo-lattice in fig. 8*a* that

$$J_1(\alpha_a; z) = \ln [\alpha_a / (1 - \alpha_a)]. \quad (108)$$

† We drop the suffix 1 from α to avoid confusion. α_a is thus the mean fraction of systems on lattice point a in state 1 ($\alpha_a \leq \frac{1}{2}$); α_{ab} is the mean fraction of pairs of systems both in state 1 on lattice points a and b .

To preserve complete generality for the calculation of $J_2(\alpha_a, \alpha_b; z)$ we must take the external fields U_a and U_b as different. We then have, for the pseudo-lattice in fig. 8b

$$\left. \begin{aligned} \alpha_a &= \mu(\nu z^{-2} + 1)/(1 + \mu + \nu + \mu\nu z^{-2}), & \mu &= \exp(-U_a/kT), \\ \alpha_b &= \nu(\mu z^{-2} + 1)/(1 + \mu + \nu + \mu\nu z^{-2}), & \nu &= \exp(-U_b/kT), \\ & & z &= \exp(\epsilon_{11}/2kT). \end{aligned} \right\} \quad (109)$$

If ν is now eliminated, the logarithm taken of μ , and the result compared with (105), we can deduce that

$$J_2(\alpha_a, \alpha_b; z) = \ln \left\{ \frac{(\alpha_a + \alpha_b - 1)z^2 + (\alpha_a - \alpha_b) + [(\alpha_a + \alpha_b - 1)^2 z^4 + 2(\alpha_a + \alpha_b - \alpha_a^2 - \alpha_b^2)z^2 + (\alpha_a - \alpha_b)^2]^{1/2}}{2\alpha_a} \right\}. \quad (110)$$

The complication in (110) arises since the equation can deal both with ferromagnetism and antiferromagnetism; for the ferromagnetic case in which $\alpha_a = \alpha_b$ a considerable simplification results. In fact in the latter case equation (105) can be identified with the well known formula in the Mayer theory expressing the absolute activity in terms of the cluster integrals, and may be written (Rushbrooke and Scoins 1955, eqn. (27))

$$\ln \mu = \ln \alpha - q \ln z - \sum_{u \geq 1} \beta_u \alpha^u. \quad (111)$$

Yvon went on to deal with higher-order terms such as triangles and squares, but only a maximum of two independent sub-lattices need usually be considered, giving two variables α_a and α_b . Thus $J_4(\alpha_a, \alpha_b, \alpha_a, \alpha_b; z)$ required in the next term for loose-packed lattices is obtained by eliminating μ and ν from the equations

$$\left. \begin{aligned} \alpha_a &= \frac{z^{-8}\mu^2\nu^2 + z^{-4}(2\mu^2\nu + \mu\nu^2) + 2z^{-2}\mu\nu + \mu^2 + \mu}{z^{-8}\mu^2\nu^2 + 2z^{-4}(\mu^2\nu + \mu\nu^2) + 4z^{-2}\mu\nu + \mu^2 + \nu^2 + 2(\mu + \nu) + 1}, \\ \alpha_b &= \frac{z^{-8}\mu^2\nu^2 + z^{-4}(\mu^2\nu + 2\mu\nu^2) + 2z^{-2}\mu\nu + \nu^2 + \nu}{z^{-8}\mu^2\nu^2 + 2z^{-4}(\mu^2\nu + \mu\nu^2) + 4z^{-2}\mu\nu + \mu^2 + \nu^2 + 2(\mu + \nu) + 1}, \end{aligned} \right\} \quad (112)$$

using (105) for α_a and α_b . Successive approximations correspond to stopping at the end of a finite number of terms of (107); the first two terms again correspond to the Bethe approximation.

Equations (105) and (107) are used by Yvon to determine the long-range order. Thus for the Ising model in the absence of a magnetic field we must look for a solution with α_a and α_b equal to $\frac{1}{2}(1+R)$ where $R \neq 0$; we know that a symmetric solution having the same partition function then exists with α_a and α_b equal to $\frac{1}{2}(1-R)$. Hence if we denote the sum of the first t terms of (107) with $\alpha_a = \alpha_b = \alpha \dots = \alpha$ by $J^{(t)}(\alpha; z)$, the long-range order is given by the equation

$$J^{(t)}[\tfrac{1}{2}(1+R); z] = J^{(t)}[\tfrac{1}{2}(1-R); z]. \quad (113)$$

Thus for the first two terms giving the Bethe approximation we find from (108) and (110) that

$$\left(\frac{1+R}{1-R}\right)^{(2/q)-1} = \frac{-1 + [1 + (R^{-2} - 1)z^{-2}]^{1/2}}{1 + [1 + (R^{-2} - 1)z^{-2}]^{1/2}} \quad \dots \quad (114)$$

Once R has been determined from (112), C can be calculated in (105), and hence α determined in the presence of a field.

For the ordered phase of an antiferromagnetic, and for alternating order generally, the two sub-lattices must be treated separately (cf. § 3.6.4), and the two functions $J^{[1]}(\alpha_a, \alpha_b; z)$ and $J^{[1]}(\alpha_b, \alpha_a; z)$ must be used. In the absence of a magnetic field, and when the sub-lattices are equivalent, the resulting equation is the same as (113), as expected. When the sub-lattices are not equivalent a different result is obtained (see e.g. Fournet 1952 b).

To determine the short-range order and internal energy, eqn. (106) must be used. This can be transformed like (107) into the form

$$\ln \alpha_{ab} = K_2(\alpha_a, \alpha_b; z) + \sum_c K_3(\alpha_a, \alpha_b, \alpha_c; z) + \sum_{c,d} K_4(\alpha_a, \alpha_b, \alpha_c, \alpha_d; z) + \dots \quad (115)$$

where the first term corresponds to occupation (single or multiple) of a pair of nearest-neighbour lattice points, the second to a triangle, . . . as before. The terms of the right-hand side of (115) can again be calculated by the use of pseudo-lattices. Thus Yvon gives, for $K_2(\alpha_a, \alpha_b; z)$ the expression

$$\ln \left\{ \frac{1 + (z^{-2} - 1)(\alpha_a + \alpha_b) - [(\alpha_a + \alpha_b - 1)^2 + 2z^{-2}(\alpha_a + \alpha_b - \alpha_a^2 - \alpha_b^2) + z^{-4}(\alpha_a - \alpha_b)^2]^{1/2}}{2(z^{-2} - 1)} \right\}, \quad \dots \quad (116)$$

and $K_4(\alpha_a, \alpha_b, \alpha_a, \alpha_b; z)$ is obtained from

$$\begin{aligned} & K_2(\alpha_a, \alpha_b; z) + K_4(\alpha_a, \alpha_b; z) \\ &= \frac{z^{-8}\mu^2\nu^2 + z^{-4}(\mu\nu^2 + \mu^2\nu) + z^{-2}\mu\nu}{z^{-8}\mu^2\nu^2 + 2z^{-4}(\mu\nu^2 + \mu^2\nu) + 4z^{-4}\mu\nu + \mu^2 + \nu^2 + 2(\mu + \nu) + 1}, \quad \dots \quad (117) \end{aligned}$$

μ and ν being derived from (105) and (107).

As might perhaps be expected the second approximation using the method of Yvon yields results identical with those of Rushbrooke and Scoins. However, in Yvon's method higher approximations can be pursued consistently for all multiply-connected configurations. The Curie temperature is that for which R , given by (113), becomes zero; hence it satisfies the relation

$$\frac{d}{dR} \{J^{[1]}[\tfrac{1}{2}(1+R); z]\}_{R=0} = 0. \quad \dots \quad (118)$$

The latter equation can be quite simply expressed in terms of the partition functions of the finite clusters which constitute $J^{[1]}(\alpha; z)$, and a series of improved estimates of the Curie temperature can be derived (Fournet 1957). These will be discussed in §§ 4.6, 4.7.1.

Although the Yvon technique may seem a little complicated it should be emphasized that once the basic formulae have been established they can be applied equally to direct or alternating order; that the method is exact in principle and a definite procedure is described for obtaining successive terms; and that further neighbour interactions can be taken into account with little additional effort (see e.g. Fournet 1952a; the latter aspect will be referred to in more detail in a subsequent publication).

4.5.3. *High temperature series expansions*

It is a well-known property of power series, all of whose coefficients are positive, that the first singularity lies on the real axis, and is hence determined by the radius of convergence of the series. Expansions of the partition function (for the Ising model) in zero field, or of the corresponding initial susceptibility in inverse powers of the temperature have all their coefficients positive, and can therefore be used to estimate the Curie temperature. The method will be effective if a sufficient number of terms is available for a reasonable estimate of the asymptotic behaviour of the coefficients to be possible.

The technique of deriving such expressions is discussed in detail in § 5. For the partition function in zero field for three-dimensional lattices we find (Domb and Sykes 1957a):

Simple cubic:

$$Z = 2(\cosh K)^3[1 + 3w^4 + 22w^6 + 192w^8 + 2046w^{10} + 24853w^{12} + \dots]$$

Body-centred cubic:

$$Z = 2(\cosh K)^4[1 + 12w^4 + 148w^6 + 2568w^8 + 53944w^{10} + \dots]$$

Face-centred cubic:

$$Z = 2(\cosh K)^6[1 + 8w^3 + 33w^4 + 168w^5 + 962w^6 + 5928w^7 + 38907w^8 + 268056w^9 + \dots]$$

$$K = J/kT, \quad w = \tanh K.$$

(119)

The first series was obtained by Wakefield (1951) who used it to estimate the Curie point of the simple cubic lattice. Wakefield derived from this series a corresponding expansion for the logarithm of the partition function, and analysed the coefficient c_n of w^{2n} in this expansion. Assuming it to be of the form n^g/w_c^n the best fit was obtained by taking $g = -3$ (only integral values were considered); using this result to approximate to the asymptotic form of c_n , Wakefield estimated the thermodynamic properties of the model at temperatures above the Curie point. In fact there were errors in the last two coefficients of Wakefield's series which have subsequently been corrected†; but his estimates of the critical point ($kT_c = 4.50J$) and thermodynamic functions seem quite reliable.

Domb and Sykes (1957b) have preferred to use the susceptibility for locating the Curie point. This series contains both odd and even terms, and

† The small error in the final term of the series given by Domb and Sykes (1957a) was pointed out by Rushbrooke and Eve (1959).

the coefficients seem to settle down more rapidly to smooth behaviour (probably because a greater variety of configurations are needed for its derivation). If we write for the initial susceptibility,

$$\chi_0 = \frac{m^2}{kT} \sum_{n=0}^{\infty} a_n K^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (120)$$

Table 2. Coefficients in the High Temperature Susceptibility Expansion

$$\chi_0 = m^2/kT \sum_{n=0}^{\infty} a_n K^n$$

Lattice	Simple quadratic	Triangular	Simple cubic	Body-centred cubic	Face-centred cubic
a_0	1.00000	1.00000	1.00000	1.00000	1.00000
$a_1/4$	1.00000	1.50000	1.50000	2.00000	3.00000
$a_2/4^2$	0.750000	1.87500	1.87500	3.50000	8.25000
$a_3/4^3$	0.541667	2.12500	2.31250	6.08333	21.8750
$a_4/4^4$	0.359375	2.28906	2.75781	10.1979	56.8906
$a_5/4^5$	0.234896	2.39141	3.28203	17.0635	146.205
$a_6/4^6$	0.149219	2.44661	3.84603	28.1373	372.766
$a_7/4^7$	0.0938836	2.46368	4.50157	46.3590	945.047
$a_8/4^8$	0.0581305	2.45098	5.22797	75.7855	2385.72
$a_9/4^9$	0.0357232		6.06678	123.820	

the coefficients a_n are given in table 2 for a number of two- and three-dimensional lattices. On physical grounds it is reasonable to assume that for sufficiently large n

$$a_n \sim n^g/K_c^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (121)$$

where g is a measure of the curvature of the reciprocal susceptibility curve near the Curie point, $g=0$ corresponding to zero curvature. This assumption can be put in the equivalent form

$$a_{n+1}/a_n \sim K_c^{-1}(1+g/n) \quad . \quad . \quad . \quad . \quad . \quad . \quad (122)$$

which is more convenient for analysis. Thus if a_{n+1}/a_n is plotted against $1/n$ the resulting curve should tend to a straight line for large n , and from the position and slope of this line T_c and g can be estimated.

In order to provide an unbiased comparison of the properties of various lattices it is convenient to introduce the factor q , and hence to estimate kT_c/qJ . Domb and Sykes thus analyzed the behaviour of

$$u_n = a_n/qa_{n-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (123)$$

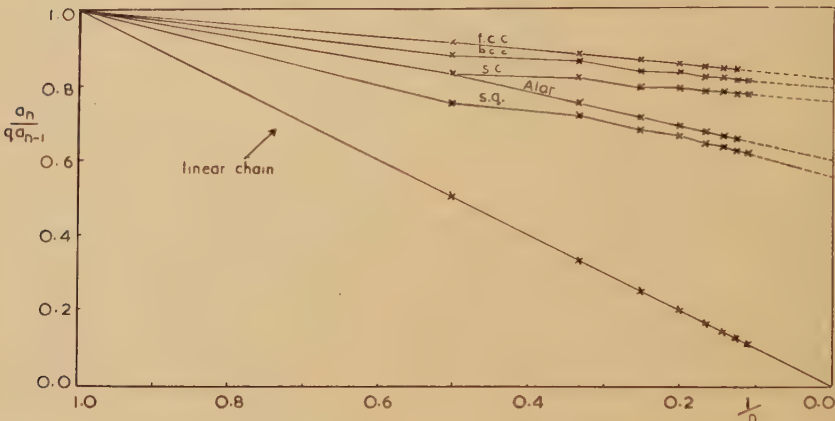
The successive values of u_n are plotted against $1/n$ in fig. 9. For any two values of n by taking the intercept of the straight line joining the corresponding values of u_n on the line $1/n=0$ an estimate is obtained for kT_c/qJ . It is found that if u_n and u_{n+1} are used, the loose-packed lattices show a

marked distinction between odd and even terms. Instead, therefore, the mean of consecutive pairs of intercepts is taken, which corresponds to using u_{n-1} and u_{n+1} . The values of these means, or of

$$\frac{1}{2}[(n+1)u_{n+1}-(n-1)u_{n-1}] \quad . \quad . \quad . \quad . \quad . \quad (124)$$

are reproduced in table 3. It will be seen that the estimates for the two-dimensional lattices based on this approach are very close to the true values. Estimates for successive n manifest a little irregular scatter, and the mean of the last two values is therefore taken as the final estimate.

Fig. 9



Estimation of the Curie point from high temperature susceptibility expansions. The values of $u_n(=a_n q a_{n-1})$ rapidly approach linearity in $1/n$, and hence the Curie point can be estimated quite accurately.

Table 3. Values of $\frac{1}{2}[(n+1)u_{n+1}-(n-1)u_{n-1}]$

Simple quadratic	Triangular	Simple cubic	Body-centred cubic	Face-centred cubic
0.58333	0.63333	0.73333	0.80357	0.82576
0.56792	0.60294	0.75676	0.80137	0.81714
0.55072	0.60785	0.75014	0.78798	0.81585
0.57884	0.60990	0.75360	0.79709	0.81580
0.56802	0.60842	0.74757	0.79175	0.81616
0.57095	0.60675	0.75328	0.79606	0.81632
0.56334	—	0.75031	0.79278	—
Mean of last two:				
0.56714	0.60759	0.75180	0.79442	0.81624
Exact value:				
0.56730	0.60682	—	—	—

Once the critical point has been determined, an asymptotic approximation to the coefficients in (119) can more readily be established, and the thermodynamic functions calculated in a manner similar to Wakefield.

4.5.4. Low-temperature expansions. Metastable approximations

The low-temperature expansion for the simple quadratic lattice in the absence of a magnetic field has all positive coefficients,

$$\Lambda = 1 + z^4 + 2z^6 + 5z^8 + 14z^{10} + 44z^{12} + 152z^{14} + \dots \quad (125)$$

and the methods of the previous section could be used to estimate the Curie point. However, this seems to be peculiar to the simple quadratic lattice, and for most three-dimensional lattices the coefficients are not consistent in sign.

For the simple cubic lattice they alternate regularly

$$\Lambda = 1 + z^6 + 3z^{10} - 3z^{12} + 15z^{14} - 30z^{16} + 101z^{18} - 261z^{20} + \dots \quad (126)$$

This series has a radius of convergence of about $z = 0.57$, whereas from the high temperature expansion we have seen that the critical point is at about $z = 0.64$. Thus the series does not converge right up to the Curie point. Wakefield (1951) endeavoured to subtract a term corresponding to the spurious singularity $z = 0.57$ which gives rise to the alternation in signs; since this is the dominant term, and the assessment of the behaviour near the Curie point depends on the remainder, the procedure is not very satisfactory.

The series for the face-centred cubic lattice is

$$\Lambda = 1 + z^{12} + 6z^{22} - 6z^{24} + 8z^{30} + 42z^{32} - 114z^{34} + 66z^{36} + 24z^{38} + 123z^{40} \\ + 134z^{42} + \dots \quad (127)$$

This is much more irregular, and it is difficult to see how any sort of extrapolation could be made.

Domb (1952) therefore suggested that the appropriate series to use in this region is the low density expansion (§ 3 (143))

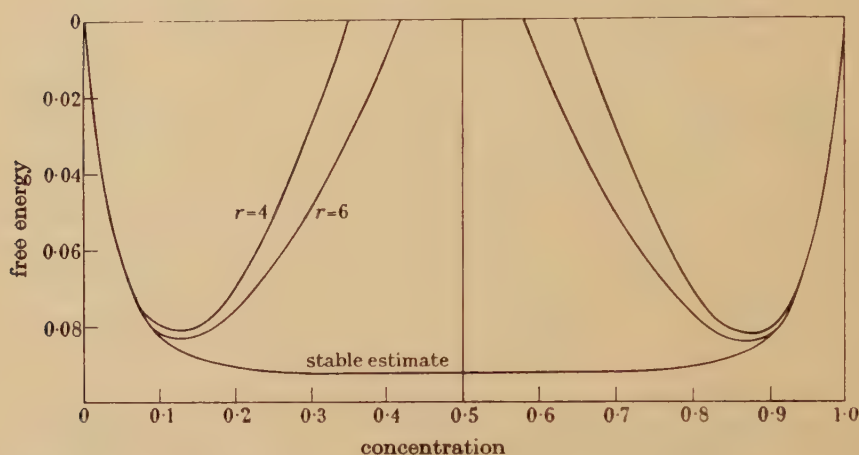
$$\Lambda = 1 + \mu f_1(z) + \mu^2 f_2(z) + \dots + \mu^t f_t(z) + \dots \quad (128)$$

The term in μ^t in this series corresponds to configurations involving t overturned spins. If this series is stopped after the term in μ^t a physical interpretation can be given to the resulting partition function Λ_t . Remembering that the partition function for the N spins of the assembly is obtained by raising the series (128) to the N th power, we see that replacing Λ by Λ_t in (128) corresponds to taking clusters of order t or less into account correctly, but ignoring all terms which involve clusters of order greater than t . Hence this represents an assembly in which clusters are allowed to grow only up to a size t , and can therefore be interpreted as a metastable assembly. This interpretation is analogous to that of Mayer in his theory of gas condensation (Mayer and Mayer 1940, p. 312). Because of this physical significance of the partial sums Λ_t , we should expect the series (128) to converge for all $\mu, z \leq 1$, although the convergence will only be rapid for sufficiently small z or μ . We have already noted (§ 3.7) that this property

has been established rigorously by Yang and Lee. It is significant in this connection that the series (128) can be used to derive high temperature expansion (§ 5.4.3).

To give an illustration of this interpretation fig. 10 shows the free energy of the partial sums as a function of concentration for the body-centred cubic lattice taking $t = 4$ and 6. It will be seen that these free energy curves have the shape characteristic of an assembly with a metastable region, and as t increases a steady series of approximations is obtained to the stable phase (it should be emphasized that the approximations are applied only in the region to the left of the first minimum or to the right of the second minimum in fig. 10, cf. § 3, fig. 42 and § 3.7.1).

Fig. 10



Metastable approximations for the b.c.c. lattice. The approximations are applied for concentrations below that corresponding to the minimum in free energy. The approximations correspond to a metastable phase.

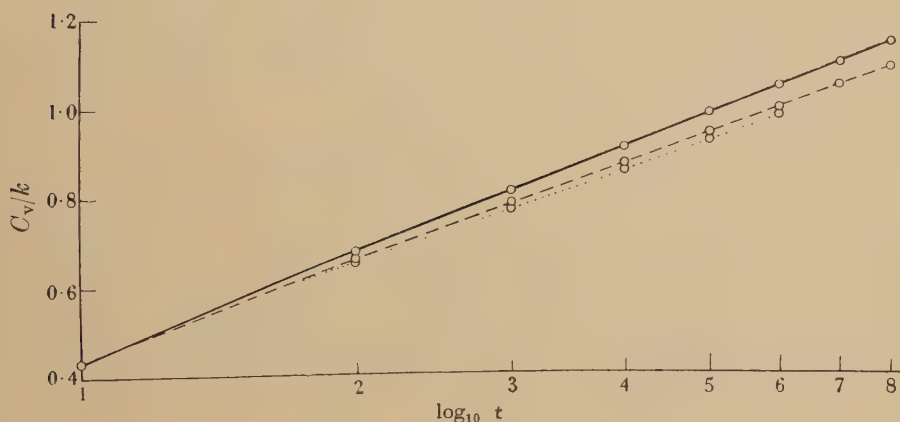
The detailed application of the method is discussed by Domb and Sykes (1956), where tables are given of polynomials $f_t(z)$ for a variety of lattices. A partial sum Λ_t is referred to as a metastable approximation of order t , and if an approximation is required to any physical quantity in the stable assembly, the corresponding quantity is determined for metastable assemblies of order t , and extrapolated to $t = \infty$. For example, by determining the maximum specific heat of a metastable assembly for a given t , and analysing its variation as a function of t , it is possible to conjecture whether the specific heat is infinite in the stable assembly. The method is then somewhat analogous to that used by Kramers and Wannier (1941) for the simple quadratic lattice before Onsager's exact work (§ 3.5.1). The known exact solutions can serve as a valuable guide to the interpretation of results, and to the estimation of the order of magnitude of errors in extrapolation. A useful feature of the method is that quantities can be compared for various

lattices at corresponding stages in the approximation, and hence any definite trends can readily be identified.

As a typical example of the application of the method, the specific heat maxima of metastable assemblies with different values of t are reproduced in Table IV for various lattices. The results are plotted in fig. 11 against $\log_{10} t$, and it is seen that they very nearly satisfy a linear relation.

As a series of values approximating to the critical point, Domb and Sykes used the temperatures of maximum specific heat of the metastable assemblies. The results are shown graphically in fig. 12. In order to compare the properties of different lattices on the same scale the estimate of kT_c/qJ is plotted as a function of $1/t$. The variation in the estimates for different values of t decreases as the coordination number of the lattice

Fig. 11



Maximum specific heats of metastable approximations. ——— simple quadratic, - - - - - simple cubic, body-centred cubic. The variation of the maximum specific heat with $\log t$ is approximately linear.

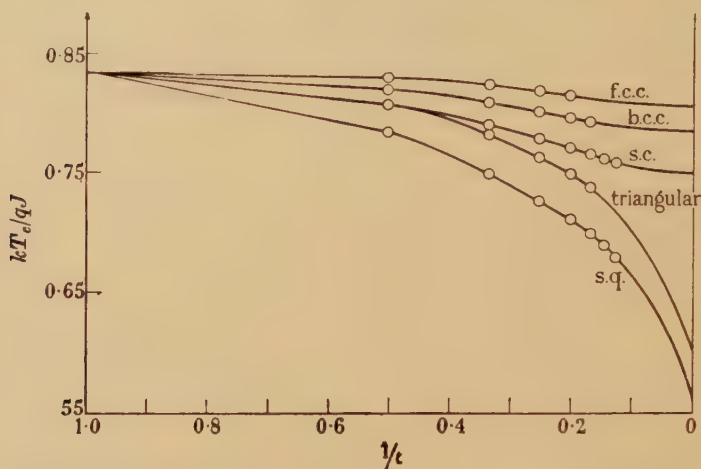
increases (a similar behaviour occurs in the high temperature estimates, fig. 9). The final estimates of the critical point obtained in this manner differed slightly ($\sim 1\%$) from the high temperature estimates. Recently Burley (1959), using the alternative possibility of locating the critical temperature as the point of disappearance of the spontaneous magnetization, secured very good agreement with the high temperature estimates.

Having located the Curie point, estimates of critical values of thermodynamic functions can be obtained by extrapolating the corresponding metastable approximations. Thus if E_t is the metastable approximation of order t for the internal energy, and $\Delta E_t = E_t - E_{t-1}$, a useful asymptotic formula for ΔE_t is A/t^h ; any successive pair of terms determines a value of h , and if the values for different pairs remain fairly constant the extrapolation

is a reasonable one. In this manner Domb and Sykes derived estimates of the critical values of energy and entropy, and these will be discussed in §4.7.2.

The method of metastable approximations depends on the provision of a smooth and steadily behaved series of approximations rather than on a good single closed-form approximation. It is exact in principle, and makes maximum use of available configurational data for the lattices considered.

Fig. 12



Estimation of the Curie point by metastable approximations. Deviations from the limiting value are less marked for three-dimensional lattices.

Table 4. Specific heat maxima of metastable assemblies ($C_{v \max}/k$)

t	Simple quadratic lattice	Triangular lattice	Simple cubic lattice	Body-centred cubic lattice	Face-centred cubic lattice
1	0.4392	0.4392	0.4392	0.4392	0.4392
2	0.6722	0.6634	0.6634	0.6582	0.6526
3	0.8168	0.8084	0.7989	0.7885	0.7819
4	0.9242	0.9137	0.8948	0.8803	0.8722
5	1.0052	0.9953	0.9671	0.9499	0.9409
6	1.0721	1.0600	1.0254	1.0059	—
7	1.1269	—	1.0740	—	—
8	1.1745	—	1.1156	—	—

4.6. Comparison of Approximate Methods

In their 1941 paper, Kramers and Wannier undertook a detailed assessment of the various approximate methods then available by comparing series expansions of the partition function of the closed-form approximations at high and low temperatures with the corresponding exact

expansions. They were concerned with the simple quadratic lattice and some examples of their results are as follows.

High temperatures:

$$\left. \begin{array}{ll} \text{Exact} & Z = 2 \left[1 + K^2 + \frac{4}{3} K^4 + \frac{77}{45} K^6 + \frac{1009}{315} K^8 + \dots \right], \\ \text{Variation} & Z = 2 \left[1 + K^2 + \frac{4}{3} K^4 + \frac{77}{45} K^6 + \frac{694}{315} K^8 + \dots \right], \\ \text{Bethe} & Z = 2 \left[1 + K^2 + \frac{1}{3} K^4 + \dots \right]. \end{array} \right\} \quad (129)$$

Low temperatures:

$$\left. \begin{array}{ll} \text{Exact} & Z = z^{-1} [1 + z^4 + 2z^6 + 5z^8 + 14z^{10} + \dots], \\ \text{Variation} & Z = z^{-1} [1 + z^4 + 2z^6 + 5z^8 + 14z^{10} + \dots], \\ \text{Bethe} & Z = z^{-1} [1 + z^4 + 2z^6 + 4z^8 + \dots]. \end{array} \right\}$$

Hence they were able to show that their own variation method represented a substantial improvement over the Bethe approximation.

Making a similar comparison for the high-temperature expansion of the simple cubic lattice following Kurata *et al.* (1953) we may write:

$$\begin{array}{ll} \text{Exact} & Z = 2(\cosh K)^3 [1 + 3w^4 + 22w^6 + 192w^8 + \dots], \\ \text{Kikuchi 3rd approximation} & \\ \text{(cube as elementary figure)} & Z = 2(\cosh K)^3 [1 + 3w^4 + 22w^6 + 189w^8 + \dots], \\ \text{ter Haar and Martin} & \\ \text{(Variation)} & Z = 2(\cosh K)^3 [1 + 3w^4 + 22w^6 + 173w^8 + \dots], \\ \text{Kikuchi 2nd approximation} & \\ \text{(square as elementary figure)} & Z = 2(\cosh K)^3 [1 + 3w^4 + 18w^6 + 147w^8 + \dots], \\ \text{Bethe} & Z = 2(\cosh K)^3, \quad (w = \tanh K). \end{array} \quad (130)$$

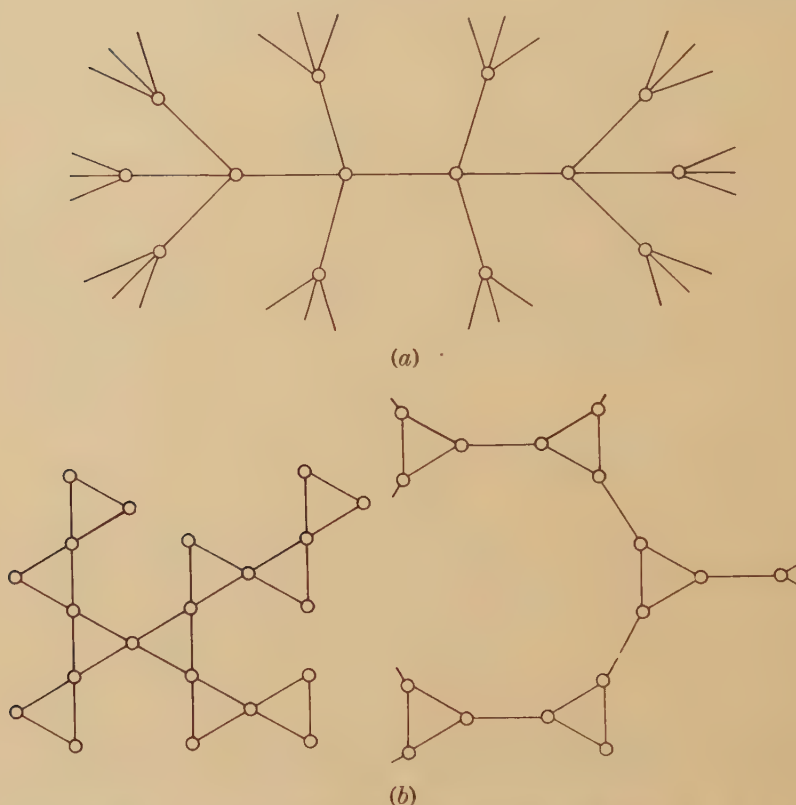
A better understanding of the nature of the various approximations is provided in a study, suggested by the above authors, of the 'configuration counting' associated with each approximation; for this purpose it is convenient to use the terminology of § 5. The Bethe approximation takes no account of closed configurations, and would be rigorously correct for a lattice of coordination number q in which there are no closed circuits, which may be called a 'Bethe Lattice' (fig. 13a). Series expansions in terms of lattice constants derived in § 5.2.10 reduce to the Bethe approximation if all the p_{ix} are put equal to zero; thus all lattice constants for a Bethe lattice depend only on q .

In the next approximation both q and p_3 are taken into account, and the remaining lattice constants taken to be zero. This approximation would be rigorously correct for a lattice in which there are no closed circuits larger than triangles (fig. 13b). It corresponds to the second approximation in the development of Rushbrooke and Scoins or Yvon. To find whether a given configuration is counted correctly or not in this approximation, all

cutting points must first be removed by the methods of §§ 5.2.4, 5.2.6 (but *not* cutting lines)[†]; the counting is correct if the resulting expression depends only on p_3 and q . For example from § 5 (9),

$$p_{6c} = \frac{9}{2}p_3^2 - 2p_{5a} - \frac{3}{2}p_3 \cdot \cdot \cdot \cdot \cdot \cdot (131)$$

Fig. 13



Pseudo-lattices for which certain approximations are exact. (a) A 'Bethe Lattice' containing no closed circuits. (b) Pseudo-lattices whose only closed circuits are triangles for which the 2nd approximation of Rushbrooke and Scoins is exact.

Therefore p_{6c} will not be correctly counted because of the p_{5a} term. By carrying out the reduction of simply-connected configurations, and putting all lattice constants other than p_3 and q equal to zero, the series expansions in § 5.2.10 can be applied to this approximation. The generalization of configuration counting to higher-order approximations of this kind is immediate.

[†] The Mayer development on which these approximations depend removes all simply-connected configurations, but not configurations which are reducible in the sense of § 5.

The Kikuchi approximation counts correctly all configurations which are open with respect to the basic figure (§4.4.3). To analyse this approximation all reducible configurations of §5 must be expressed in terms of irreducible lattice constants; if these expressions involve only configurations contained in the basic figure, the counting will be correct. Thus from §5 (11) both p_{5a} and p_{6c} will be correctly counted by the Kikuchi approximation using a triangle as basic figure, and hence this approximation is better than the corresponding approximation of the previous paragraph. Similarly for a loose packed lattice with a square as basic figure p_{7a} and p_{8h} will be correctly counted. However, when we look at simple polygons, the individual space types must be examined. Thus considering hexagons on the simple cubic lattice, the first two space types in §5, fig. 6, will be counted, but not the last one; hence the coefficient 18 instead of 22 of w^6 in (130) for this approximation. When a cube is taken as basic figure all hexagons are correctly counted; but when we examine octagons in §5, fig. 7, all space types except (i) are correctly counted, and the coefficient of w^8 is 189 instead of 192.

The approximations of §§4.5.3, 4.5.4 make direct use of exact series expansions as far as they are available, and depend on the smooth convergence of partial sums. For the Ising model of a ferromagnetic they seem particularly suitable; for the antiferromagnetic in a magnetic field (§3.7), where terms alternate in sign, they cannot be readily applied. It was noted by Domb and Sykes (1957 b) that high and low-temperature estimates of the Curie point differed slightly. The properties of the disordered state are simpler than those of the ordered state, and for most approximations the Curie point can be more readily located from the disordered state. It is likely that this is also true of series expansions, and thus high temperature estimates are probably more reliable (this is also the conclusion of Burley (1959)). This would mean that the curve of metastable estimates (fig. 2) passes through a minimum and turns up slightly in the limit. Dr. M. F. Sykes has suggested (privately) that the use of the series for $\ln \Lambda$ instead of Λ in (128), corresponding more precisely to the Mayer theory, might lead to a more uniform approach to the critical point.

The reliability of the closed form approximations would be substantially increased if they could be made to supply a steadily behaved series of values of any thermodynamic quantity to be estimated. The initial improvement achieved by the Kikuchi approximation is striking, but it is difficult to proceed to high approximations. The method of Rushbrooke and Scoins as formulated at present can only make use of homogeneous configurations, and hence it is not possible to provide systematic improvements. The method of Yvon can take all configurations into account, and the formulation of a series of successive approximations to the critical point was undertaken by Fournet (1957). However, only three terms of this series were calculated, and although the results of extrapolation seem to provide better estimates than any other single closed form approximation, we do not think that they are as reliable as the results of direct series

expansions in §§ 4.5.3, 4.5.4, which make use of several more terms. The results of Fournet might well be extended with the aid of the configurational data of § 5.

4.7. *Physical Properties of the Three-dimensional Ising Model*

Before discussing in detail the characteristic features of the three-dimensional Ising model we shall briefly summarize the main conclusions to which we have been led. The specific heat of the three-dimensional model seems to remain infinite at the Curie point, but its detailed shape is appreciably different from the Onsager curve in two dimensions. The 'tail' is far smaller, showing that most of entropy change of the assembly takes place in the temperature region below the Curie point; this is in far better agreement with experimental observations of specific heat anomalies.

The dimension of the lattice is of primary significance in determining the properties of a model, and the coordination number plays only a small part. The differences between lattices of the same dimension are thus only of secondary importance. As an example of this, the two-dimensional triangular lattice and the three-dimensional simple cubic lattice both have coordination number 6; but the properties of the former are very similar to the honeycomb lattice of coordination number 3, and those of the latter to the face-centred cubic lattice of coordination number 12.

Simple closed form approximations (such as the mean field and Bethe approximations) are closer to the true solution in three dimensions than in two dimensions. Hence the inverse susceptibility above the Curie point is more nearly linear in three dimensions than in two dimensions, and the spontaneous magnetization curve at the Curie point is less steep.

4.7.1. *Position of the Curie point*

It is interesting to compare the values of kT_c/qJ for various lattices as estimated by different approximations (table 5); this quantity is considerably more sensitive than z_c [$=\exp -(J/kT_c)$] for larger coordination numbers. For the mean field approximation it is 1 for all lattices. For the Bethe approximation, (28), it depends on q only, being zero for $q=2$ and increasing steadily to the mean field value as $q \rightarrow \infty$. The Kikuchi approximation takes into account the first few closed configurations, and a marked separation becomes manifest between the triangular and simple cubic lattices.

The first four approximations which are of closed form all overestimate the Curie temperature. The remainder depend on some form of extrapolation, and may either overestimate or underestimate it. Fournet's results, based on the method of Yvon, use the first three stages of the approximation, which are fitted for $t=1, 2, 3$ to a second degree polynomial in $1/t$; this is then extrapolated to $1/t=0$. The value for the simple cubic lattice seems appreciably better than those for the body-centred cubic and face-centred cubic lattices. The estimates of the metastable approximations and high-temperature series expansions are quite close to one another, and for the

reasons stated in the previous section we have adopted the latter as final estimates. Polynomial fitting in $1/t$ was not considered to be the most suitable method of extrapolation since it pays too much attention to slight irregularities. Instead some suitable asymptotic formula was postulated, the parameters of which were fitted from the results of successive approximations (§§ 4.5.3, 4.5.4).

Table 5. Approximations to the Curie Point
(Recorded values are $t_c = kT_c/qJ$)

Lattice approximation	Simple quadratic	Triangular	Simple cubic	Body-centred cubic	Face-centred cubic
Mean field	1	1	1	1	1
Bethe and quasi-chemical	0.721	0.822	0.822	0.869	0.914
Rushbrooke and Scoins	0.657	0.744	0.794	0.835	0.882
Kikuchi (2nd approximation)	0.606	0.653	0.768	0.869	0.835
Yvon-Fournet (extrapolation)	0.578	0.622	0.761	0.865	0.704
Metastable approximations	—	—	0.748	0.784	0.805
High temperature susceptibility series	0.567	0.608	0.752	0.794	0.816
Exact	0.567	0.607	—	—	—

4.7.2. Critical values of thermodynamic functions

The estimates of critical values of energy and entropy provided by a given approximation are less accurate than corresponding estimates of the critical temperature, since a double process of approximation is involved. (Some typical results are compared in table 6.) A clear improvement can again be noted in passing from a two-dimensional to a three-dimensional model.

The metastable estimates have been evaluated at the values of the critical point given by the high temperature expansions (table 5). Critical values of Λ and E are determined by noting the size of successive approximations for the known values of t and fitting the difference between the t th and $(t-1)$ th terms to A/t^h ; any successive pair of terms determines a value of h and if the values for different pairs remain fairly constant it is reasonable to extrapolate to $t = \infty$. (Further details are given in Domb and Sykes (1956)). The results are in good agreement with independent estimates based on high temperature series expansions.

We have collected in table 7 exact critical values for two-dimensional lattices and final estimates for three-dimensional lattices. In order to compare the difference between the specific heat curves for the various

lattices, it is convenient to take T_c as a unit of temperature, and consider C_v as a function of τ ($=T/T_c$). Then

$$\left. \begin{aligned} S_c &= \int_0^1 \frac{C_v}{\tau} d\tau, \\ S_\infty - S_c &= \int_1^\infty \frac{C_v}{\tau} d\tau, \end{aligned} \right\} \dots \dots \dots (132)$$

Table 6. Approximations to Critical Values

Lattice approximation	Simple quadratic		Simple cubic		Face-centred cubic	
	$-E_c/J$	S_c/k	$-E_c/J$	S_c/k	$-E_c/J$	S_c/k
Mean field	0	0.693	0	0.693	0	0.693
Bethe or quasi-chemical	0.667	0.580	0.600	0.633	0.545	0.668
Kikuchi (2nd approximation)	1.123	0.428	0.857	0.587	1.200	0.618
Metastable approximations	1.405	0.311	1.015	0.553	1.546	0.589
High temperature series extrapolations	1.406	0.311	1.071	0.541	1.464	0.597
Exact	1.414	0.306	—	—	—	—

Table 7.

Lattice structure	q	$kT_c/qJ(=t_c)$	S_c/k	$(S_\infty - S_c)/k$	$(E_c - E_0)/kT_c$	$(E_\infty - E_c)/kT_c$
linear chain	2	0	0	0.693	0	∞
honeycomb	3	0.506	0.265	0.428	0.227	0.761
simple quadratic	4	0.567	0.306	0.387	0.258	0.623
triangular	6	0.607	0.330	0.363	0.275	0.549
simple cubic	6	0.752	0.541	0.152	0.428	0.237
body-centred cubic	8	0.794	0.586	0.107	0.460	0.169
face-centred cubic	12	0.816	0.597	0.096	0.463	0.150

so that a tabulation of S_c and $S_\infty - S_c$ for various lattices enables us to compare the magnitude of the specific heat curves below and above the Curie point. The sum of the two terms, S_∞ , is the same for all lattices, and is equal to $k \ln 2$ ($=0.6931k$). For a linear chain the Curie point is at $T=0$, and all of the specific heat is above the Curie point. As the coordination number increases, more and more of the specific heat curve moves below the Curie point, until for $q = \infty$ the mean field approximation shows us that all of the specific heat curve is below the Curie point.

Critical values of the entropy and the total entropy change in the assembly are particularly useful quantities for testing the validity of a given model; direct comparison with experiment is possible since these values do not depend on the interaction energy.

The difference in passing from a two to a three-dimensional lattice is quite striking. For all the two-dimensional lattices more than 50% of the entropy change occurs above the Curie point, but for the simple cubic lattice the 'tail' is very much reduced, even though this lattice has the same coordination number as the triangular lattice. For the body-centred cubic and face-centred cubic lattices the 'tail' is even smaller, and this must lead to a specific heat curve in closer agreement with experimental curves.

The difference between two- and three-dimensional assemblies is even more evident if we look at the values of

$$\left. \begin{aligned} (E_c - E_0)/kT_c &= \frac{1}{k} \int_0^1 C_v d\tau, \\ -E_c/kT_c &= \frac{1}{k} \int_1^\infty C_v d\tau. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (133)$$

The sum of the two terms, $-E_0/kT_c$, is not constant, but decreases from ∞ to a limiting value of $1/2$ as $q \rightarrow \infty$. These terms represent directly the areas under the specific heat curve below and above the Curie point, and the decrease in the 'tail' is clearly demonstrated as the coordination number increases.

4.7.3. The specific heat curve

In the previous section we have made use of critical values to draw some general conclusions regarding the dependence of the specific heat curve on lattice structure. We shall now attempt a more detailed description of its behaviour.

At sufficiently low temperatures the specific heat is given by the first term of the low-temperature expansion and we have

$$C_v/k \simeq \left(\frac{2qJ}{kT} \right)^2 \exp(-2qJ/kT). \quad . \quad . \quad . \quad . \quad (134)$$

Taking a reduced temperature, τ , as in the previous section, we may write this in the form

$$C_v/k \simeq \left(\frac{2}{\tau t_c} \right)^2 \exp(-2/\tau t_c). \quad . \quad . \quad . \quad . \quad (135)$$

Hence, for a given τ , C_v increases as t_c increases, i.e. as we pass down the rows in table 7.

Correspondingly, at sufficiently high temperatures the specific heat is given by

$$C_v/k \simeq \frac{q}{2} \left(\frac{J}{kT} \right)^2, \quad . \quad . \quad . \quad . \quad . \quad (136)$$

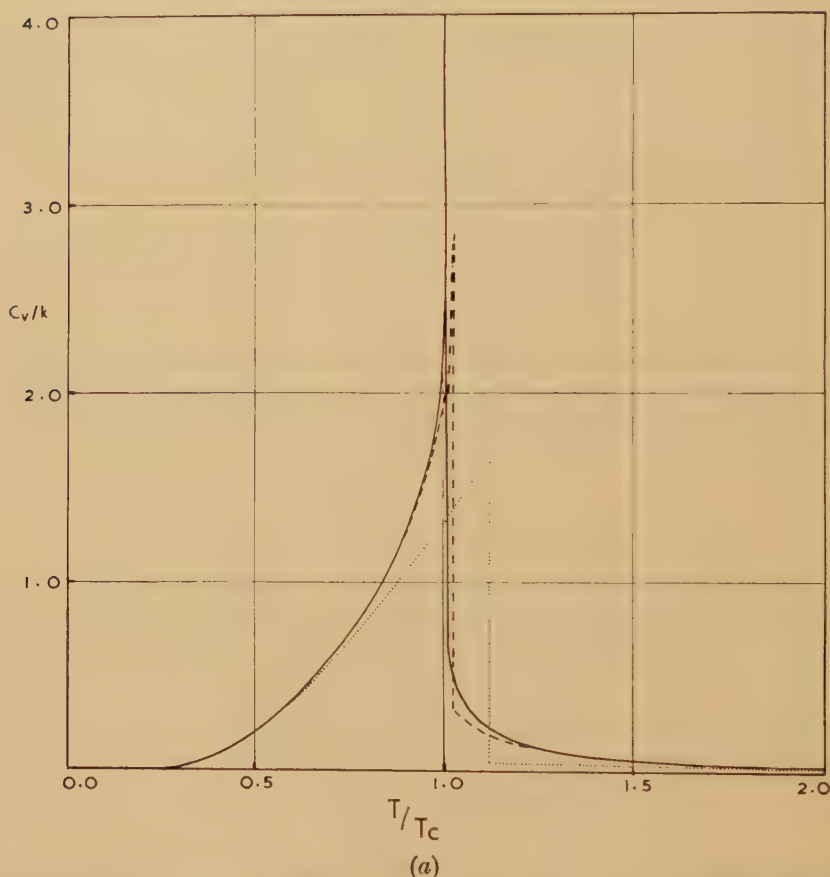
or, in reduced units, by

$$C_v/k \simeq 1/2 q \tau^2 t_c^2 \quad . \quad . \quad . \quad . \quad . \quad (137)$$

Hence, for a given τ , C_v decreases as q or t_c increase, and this supports the conclusions of the previous section.

We have seen in § 4.5.4 that metastable approximations indicate that the specific heat remains infinite in three dimensions. For the purpose of detailed comparison between two and three-dimensional lattices Domb and Sykes (1957 c) used high temperature series expansions for the triangular and face-centred cubic lattices; odd and even terms occur in the

Fig. 14



Comparison of specific heat curves given by various approximations.
 (a) Face-centred cubic lattice. ——— Based on series expansions.
 ----- Kikuchi approximation. First-order Beth approximation.

expansions for these close-packed lattices, and hence more terms are available for analysis. The expansions in reduced form are

Triangular :

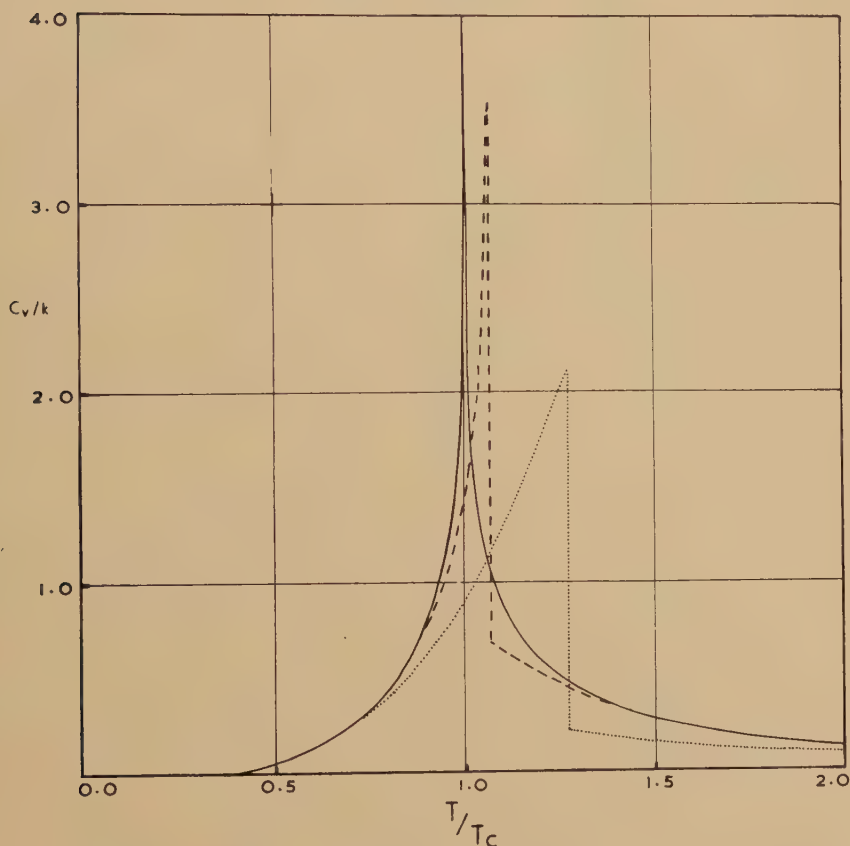
$$C_v/k = 0.2263 \kappa^2 (1 + 1.0986 \kappa + 0.8298 \kappa^2 + 0.5525 \kappa^3 + 0.4021 \kappa^4 + 0.3384 \kappa^5 + 0.2971 \kappa^6 + 0.2614 \kappa^7 + \dots).$$

Face-centred cubic :

$$C_v/k = 0.06257 \kappa^2 (1 + 0.8169 \kappa + 0.6778 \kappa^2 + 0.5680 \kappa^3 + 0.4818 \kappa^4 + 0.4190 \kappa^5 + 0.3725 \kappa^6 + 0.3364 \kappa^7 + \dots) \quad (\kappa = 1/\tau).$$

(138)

In comparing these two expansions we may say roughly that the term outside the parentheses represents the magnitude of the 'tail' of the specific heat curve, and the term inside the parentheses represents the shape of the curve, particularly near the Curie point. It will be seen that the magnitude of the tail is much smaller for the face-centred cubic lattice.

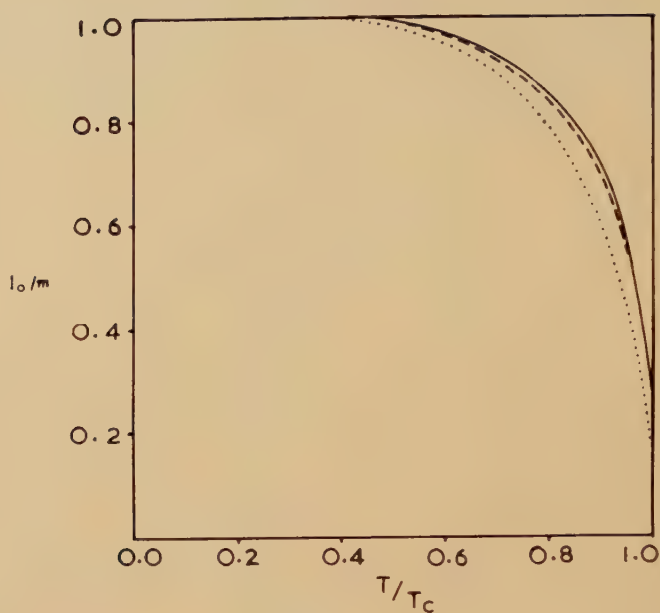
Fig. 14 (*continued*)

(b)

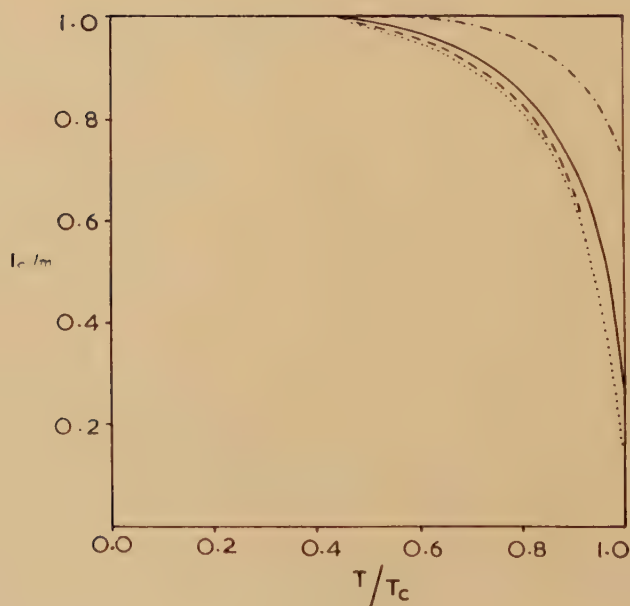
Comparison of specific heat curves given by various approximations.
 (b) (After Onsager) simple quadratic lattice. ——— Exact.
 - - - - - Kramers and Wannier variation (\equiv Kikuchi). Bethe.

But it will also be noted that the coefficients decrease less rapidly for the face-centred cubic lattice and the specific heat curve is therefore sharper (and is thus certainly infinite). By analysing the magnitude of the n th coefficient in the face-centred cubic expansion Domb and Sykes obtained indications of an asymptotic behaviour of the specific heat of the form $C_v/k \sim (1 - \kappa)^{-1/b}$ ($b \geq 4$).

Fig. 15



(a)



(b)

Estimates of the spontaneous magnetization for three-dimensional lattices. (a) Comparison of approximations for the simple cubic lattices, ——— Metastable, ——— Kikuchi, Bethe. (b) Comparison of spontaneous magnetization curves for various lattices; ——— simple cubic, ——— body-centred cubic, face-centred cubic. (Two-dimensional simple quadratic for comparison — · — · —)

On the low temperature side the estimation of the specific heat is less reliable, and metastable approximations have been used. The final estimate of the specific heat curve for the face-centred cubic lattice is reproduced in fig. 14 (*a*) together with estimates of other approximations. A similar comparison for the simple quadratic lattice was given in the classic paper by Onsager (1944) and is shown in fig. 14 (*b*). The improvement in the approximations in going from two to three dimensions will again be noted.

4.7.4. *The spontaneous magnetization*

The dependence of the spontaneous magnetization on lattice structure has recently been carefully investigated by Burley (1959). Near the Curie point the mean field and Bethe approximations both lead to the conclusion $I_0 \simeq A(1 - T/T_c)^{1/2}$ (see (9) and (31)). However, for two dimensional lattices the exact solution (§§ 3.5.1, 3.5.4) gives $I_0 \simeq (1 - T/T_c)^{1/8}$, so that the approximations are seriously in error. Burley used the Kikuchi approximation and the metastable method to estimate the spontaneous magnetization for three-dimensional lattices. The difference between these two estimates was very small (fig. 15 *a*). He found that the curve of spontaneous magnetization approaches the axis at T_c less steeply in three dimensions than in two dimensions, the power of $(1 - T/T_c)$ being estimated as between $1/2$ and $1/4$; also the standard approximations are more accurate in three than in two dimensions. These results are illustrated in figs. 15 *a*, *b*. Thus we find again that the dimension of a model is the major factor in determining the shape of the spontaneous magnetization curve, the difference in crystal lattice leading only to a 'fine structure' variation.

The conclusion regarding the steepness of the curve also results from an alternative method of using series expansions due to Park (1956) who attempted to approximate to the known terms of the expansion by a closed algebraic expression. Park's estimate of the power of $(1 - T/T_c)$ for the spontaneous magnetization in three dimensions was initially $17/64$, but was subsequently modified to $3/16$ (private communication).

4.7.5. *The high-temperature susceptibility*

The initial susceptibility above the Curie point will be discussed in detail in a subsequent publication. We here quote the result that the inverse susceptibility is less curved in the neighbourhood of the Curie temperature for a three-dimensional model than for a two-dimensional model (and hence closer to the linear result of the mean field approximation (11)). In two dimensions $\chi_0 \simeq A(1 - T_c/T)^{-7/4}$ near the Curie point (this has recently received rigorous justification by Fisher (1959)); in three dimensions the corresponding estimate is $\chi_0 \simeq A(1 - T_c/T)^{-5/4}$ (Domb and Sykes 1957 *b*).

It has been pointed out by Rice (1954) that the infinity in specific heat corresponds only to an incompressible lattice; if the lattice is compressible a first-order transition results (see also Domb (1956)).

Notation for § 4

H_0 parameter in mean field approximation: $\xi = mH_0/kT$.

$\delta = (N_2 - N_1)/N = \alpha_2 - \alpha_1$.

H_1 = parameter in Bethe approximation; $\mu_1 = \exp(-2mH_1/kT)$.

\mathcal{H}_q, Z_q interaction energy and partition function of an elementary cluster consisting of a central spin and its q nearest neighbours.

$x_1, x_2; y_1, y_2, y_3; z_1, z_2, z_3, z_4, z_5, z_6; w_1, w_2, w_3, w_4, w_5, w_6$;

parameters in Kikuchi approximation

L number of assemblies in ensemble for Kikuchi approximation

$$X_L = \prod_{i=1}^2 (x_i L)!, \quad Y_L = \prod_{i=1}^3 (y_i L)!, \quad Z_L = \prod_{i=1}^6 (z_i L)!, \quad W_L = \prod_{i=1}^6 (w_i L)!$$

Cluster Sum Theory

$f = z^{-2} - 1, f_{ij}$ defined by (74), $b_i(z)$ by (80), $\beta_u(z)$ by (83) $H_{tx}(\alpha_1, z)$ by (86).

Method of Yvon

α_a, α_b mean fraction of systems on lattice points a, b in state 1. α_{ab} mean fraction of pairs of systems on lattice points a, b both in state 1.

$J_1(\alpha_a; z), J_2(\alpha_a, \alpha_b; z), J_3(\alpha_a, \alpha_b, \alpha_c; z) \dots$ defined by (107); $J^{(1)}(\alpha; z)$ see (113).

$K_2(\alpha_a, \alpha_b; z), K_3(\alpha_a, \alpha_b; z)$ defined by (115).

U_a, U_b external field at lattice points a, b ; $\mu = \exp(-U_a/kT)$,
 $\nu = \exp(-U_b/kT)$.

a_n coefficient of K^n is series for susceptibility (120), $a_n \sim n^q/Kc^n$.

$u_n = 2a_n/qa_{n-1}$.

Λ_t = sum of terms of partition function up to and including term in μ^t .

$\tau = T/T_c$; $\kappa = 1/\tau$.

REFERENCES

- BELL, G. M., 1952, *Phil. Mag.*, **43**, 127.
 BERLIN, T. H., and KAC, M., 1952, *Phys. Rev.*, **86**, 821.
 BETHE, H. A., 1935, *Proc. roy. Soc. A*, **216**, 45.
 BRAGG, W. L., and WILLIAMS, E. J., 1934, *Proc. roy. Soc. A*, **145**, 699.
 BURLEY, D. M., 1959, Thesis, University of London (to be published).
 COWLEY, J. W., 1950, *Phys. Rev.*, **77**, 669.
 DOMB, C., 1952, *C.R. 2e Reunion Chimie Physique*, Paris, p. 192; 1956, *J. chem. Phys.*, **25**, 783.
 DOMB, C., and SYKES, M. F., 1956, *Proc. roy. Soc. A*, **235**, 247; 1957 a, *Phil. Mag.*, **2**, 733; 1957 b, *Proc. roy. Soc. A*, **240**, 214; 1957 c, *Phys. Rev.*, **108**, 1415.
 FIRGAU, U., 1941, *Ann. Phys., Lpz.*, **40**, 295.
 FISHER, M. E., 1959, *Physica*, **25**, 521.
 FORD, G. W., and UHLENBECK, G. E., 1956, *Proc. nat. Acad. Sci.*, **42**, 122; 1957, *Ibid.*, **43**, 163.

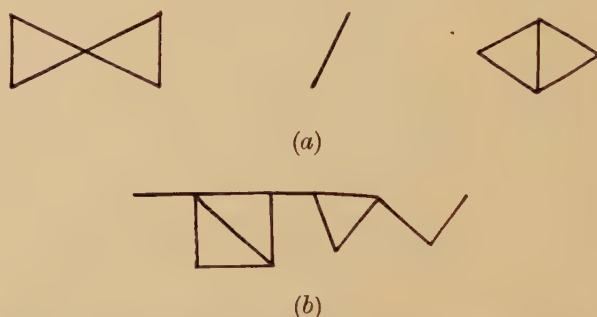
- FOSDICK, L. D., and JAMES, H. M., 1953, *Phys. Rev.*, **91**, 1131.
- FOURNET, G., 1952 a, *J. Phys. Radium*, **13**, 14; 1952 b, *C. R. 2e Reun. Chim. Phys.*, p. 199; 1953, *J. Phys. Radium*, **14**, 226, 374; 1957, *Acta Met.*, **1**, 383; *J. Phys. Radium*, **18**, 663.
- FOWLER, R. H., and GUGGENHEIM, E. A., 1940, *Proc. roy. Soc. A*, **174**, 189.
- FUCHS, K., 1942, *Proc. roy. Soc. A*, **179**, 340.
- GUGGENHEIM, E. A., 1935, *Proc. roy. Soc. A*, **148**, 304; 1952, *Mixtures* § 4.14, Oxford.
- GUGGENHEIM, E. A., and MCGLASHAN, M. L., 1951, *Proc. roy. Soc. A*, **206**, 335.
- HEISENBERG, W., 1928, *Z. Phys.*, **49**, 619.
- HIJMAN, J., and DE BOER, J., 1955, *Physica*, **21**, 471, 485, 199; 1956, *Ibid.*, **22**, 387.
- HILL, T. L., 1950, *J. chem. Phys.*, **18**, 988.
- KASTELEIJN, P. W., 1956, *Physica*, **22**, 387.
- KASTELEIJN, P. W., and VAN KRANENDONK, J., 1956, *Physica*, **22**, 317, 367.
- KATSURA, S., 1958, *Prog. Theor. Phys.*, **20**, 192.
- KIKUCHI, R., 1951, *Phys. Rev.*, **81**, 988.
- KRAMERS, W. A., and WANNIER, G. H., 1941, *Phys. Rev.*, **60**, 252, 263.
- KURATA, M., KIKUCHI, R., and WATARI, T., 1953, *J. chem. Phys.*, **21**, 434.
- LEVITAS, A., and LAX, M., 1958, *Phys. Rev.*, **110**, 1016.
- LI, Y. Y., 1949, *Phys. Rev.*, **76**, 972; *J. chem. Phys.*, **17**, 447.
- MAYER, J. E., and Mayer, M. G., 1940, *Statistical Mechanics* (New York: John Wiley).
- ONSAGER, L., 1944, *Phys. Rev.*, **65**, 117.
- PEIERLS, R., 1936, *Proc. Camb. phil. Soc.*, **32**, 477.
- PARK, D., 1956, *Physica*, **22**, 932.
- PRIGOGINE, I., SAROLEA, L. M., and VAN HOVE, 1952, *Trans. Faraday Soc.*, **48**, 485.
- RICE, O. K., 1954, *J. chem. Phys.*, **22**, 1935.
- RIDDELL, R. J., and UHLENBECK, G. E., 1953, *J. chem. Phys.*, **21**, 2056.
- RUSHBROOKE, G. S., 1949, *Statistical Mechanics* (Oxford: 1949).
- RUSHBROOKE, G. S., and EVE, J., 1959, private communication.
- RUSHBROOKE, G. S., and SCOINS, I., 1955, *Proc. roy. Soc. A*, **230**, 74.
- TEMPERLEY, H. N. V., 1959, *Proc. Phys. Soc. Lond.*, **74**, 183.
- TER HAAR, D., and MARTIN, B., 1950, *Phys. Rev.*, **77**, 721.
- WAKEFIELD, A. J., 1951, *Proc. Camb. phil. Soc.*, **47**, 419, 799.
- WEISS, P., 1907, *J. Phys.*, **6**, 661.
- WEISS, P. R., 1948, *Phys. Rev.*, **74**, 1493.
- YANG, C. N., 1945, *J. chem. Phys.*, **13**, 66.
- YVON, J., 1937, *Actualite Scientifiques et Industrielles* (Paris: Herman & Cie), No. 542; 1945, *Cah. Phys.*, No. 28 (1948), Nos. 31, 32.
- ZERNIKE, F., 1940, *Physica*, **7**, 565.

§ 5. CONFIGURATIONAL PROBLEMS AND SERIES EXPANSIONS†

5.1. *General Introduction*

Perturbation expansions have been used widely in astronomy and physics to calculate the effect of small changes in problems for which exact solutions are available. However, the derivation of substantial numbers of terms of a perturbation expansion, and the use of such an expansion as a source of exact information have been more restricted. A significant example of the latter kind is the Mayer theory of the condensation of gases, and recent developments in quantum electrodynamics provide a striking additional example. In classifying the contributions of higher order terms one is naturally led to a consideration of the various types of linear graph which can be constructed from a given number of points and lines. Some general references on the theory of linear graphs are given at the end of the chapter.

Fig. 1



Classification of linear graphs as 'separated' or 'connected'. (a) A separated graph of 12 lines; (b) A connected graph of 12 lines.

The application of linear graphs to the Mayer theory has been particularly studied by Uhlenbeck and his collaborators. In this theory each topological type of graph leads to a particular cluster integral, and Riddell and Uhlenbeck (1953) solved the combinatorial problem of determining the number of graphs of each type. The problem of the evaluation of the resulting integrals for any reasonable physical potential remains extremely formidable.

We shall classify the graphs which can be formed with p points and l lines into groups. We first distinguish between

(A) *Separated graphs* which consist of two or more graphs which are not connected together (fig. 1a) and

(B) *Connected graphs* (fig. 1b).

We now sub-divide (b) into

(i) 'Stars'—multiply-connected graphs (fig. 2a).

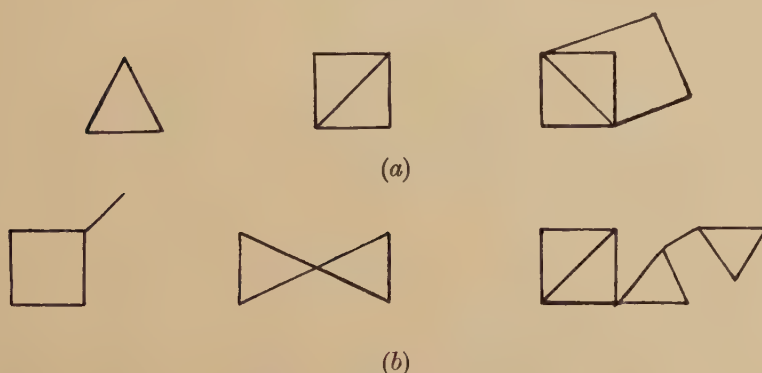
(ii) 'Trees'—graphs which are not multiply-connected (fig. 2b).

† This chapter has been written in collaboration with Dr. M. F. Sykes.

By *multiply-connected* we mean that at least two independent paths which cross only at the end points connect every pair of points of the graph. The graphs of group (ii), which are not multiply-connected, must contain at least one *articulation point* or *cutting point*, which is a point where the graph could be cut into two or more separated graphs by cutting all lines going to this point. This group may be further sub-classified into

- (a) *Cayley trees* (Cayley 1889–98) which are connected graphs of p points and $(p - 1)$ lines containing no closed circuits (fig. 3a).
- (b) *Husimi trees* (Husimi 1950) which are built up similarly out of simple polygons so that no line lies on more than one closed circuit (fig. 3b). A *pure* Husimi tree is one which contains only one type of polygon.
- (c) *Star trees*. The remaining graphs with articulation points in which the units are more complex than simple polygons (fig. 3c).

Fig. 2



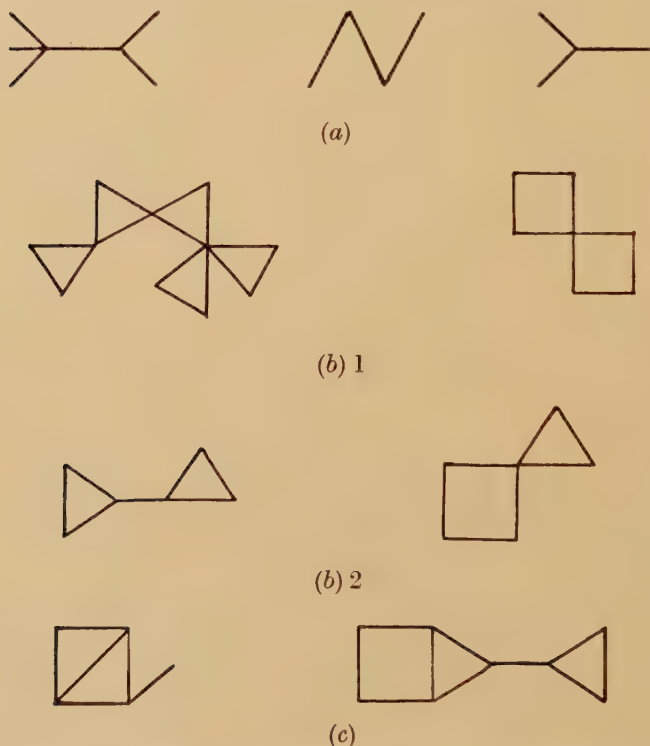
Sub-classification of connected graphs. (a) Multiply-connected graphs or 'stars'; (b) Graphs which are not multiply-connected and therefore possess a cutting point ('trees').

For the Mayer theory all the integrals which arise can be reduced to integrals of stars; some of these (e.g. simple polygons) can be evaluated easily, but in general the evaluation is not possible beyond three or four terms. The problems with which we have been concerned are confined to crystal lattices, and the cluster integrals are replaced by cluster sums. If interactions of all neighbours were taken into account, these sums would be almost as difficult to evaluate as the cluster integrals; the simplification in the lattice model arises largely since it is a reasonable physical approximation to take account only of nearest-neighbour interactions. The basic problem is then to count the number of ways in which particular types of configuration can occur on a given lattice (using only nearest-neighbour links) and this combinatorial problem replaces the evaluation of cluster integrals. Also for such lattices many types of cluster configuration cannot occur, and hence the expansion can be followed for a substantial number of additional terms.

It is convenient to consider separately the topological problems arising from low-temperature and high-temperature expansions. For the Ising model the low-temperature (or low-density) expansions can be put into a form exactly analogous to the Mayer theory; the high-temperature series can be deduced from them, since the two expansions are not independent.

However, it is important to develop direct methods of evaluating high-temperature series for application to more general forms of interaction in crystals, and even for the Ising model many more terms can be evaluated by these direct methods for particular problems.

Fig. 3



Sub-classification of trees. (a) Cayley trees which involve no closed circuits; (b) 1, Pure Husimi trees which involve only one type of polygon; (b) 2, Mixed Husimi trees which involve lines and simple polygons; (c) More general trees.

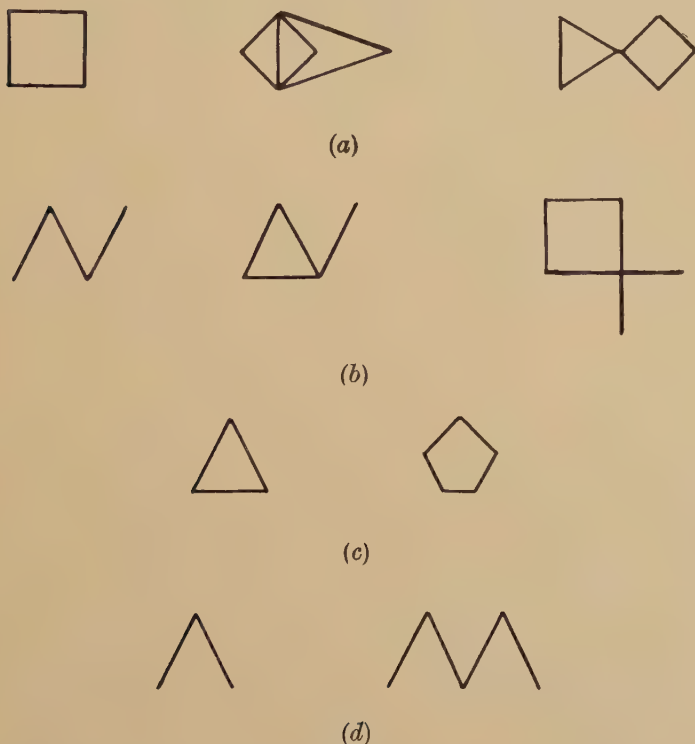
5.1.1. High-temperature configurations

The form of the high-temperature expansions has been established for the Ising model in § 3.6.2. The topological problem is one of 'line counts', i.e. of classifying and enumerating all configurations of l lines which can occur on the lattice. The configurations may be sub-divided as in the previous section into connected and separated configurations; but whilst

in the Mayer theory the separated configurations are readily eliminated, for crystal configurations they are of considerable significance and are difficult to enumerate.

For the Ising model in the absence of a magnetic field the configurations of interest are closed configurations all of whose vertices are even (i.e. are the meeting point of an even number of lines) (fig. 4*a*). For the susceptibility in zero field the corresponding configurations are those with exactly two odd vertices (fig. 4*b*). Other line configurations of particular interest are simple closed polygons p_i (fig. 4*c*) and simple chains c_i (fig. 4*d*).

Fig. 4



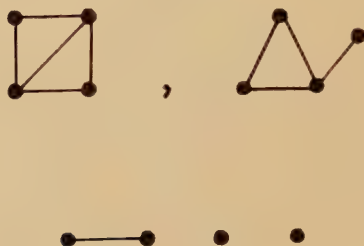
Typical high-temperature configurations. (a) No-field configurations for the Ising model; (b) Susceptibility configurations for the Ising model; (c) Polygons; (d) Simple chains.

We shall be mainly concerned with lattices in which all points and bonds are equivalent, which we shall call *regular* lattices. It will be assumed that the lattices are connected cyclically so that end effects are eliminated. The number of configurations of a given type which can be arranged on a lattice will be referred to as the lattice constant for the particular type. More specifically we shall define lattice constants *per site* so that if p_3 is the lattice constant for triangles, then the complete lattice contains Np_3 triangles. We shall describe as a *closed configuration*

a connected graph in which each vertex is the meet of at least two lines. Closed configurations of l lines other than simple polygons will be denoted by suffixes $p_{1a}, p_{1b}, p_{1c} \dots$. Separated configurations will be denoted by brackets containing the connected portions, e.g. $[p_3, p_4]$ for a separated triangle and quadrilateral, and $[p_3, p_3, p_3]$ for three separated triangles.

All lattice constants for regular lattices can be expressed algebraically in terms of a selected number of 'irreducible' constants. However, the concept of irreducibility for lattice configurations differs from that used in the Mayer theory. For example, configurations consisting of two simple polygons with one side in common (e.g. p_{5a}, p_{6b} , Appendix III, table A) are reducible in our sense but not in the Mayer theory; for this reason we have preferred the term 'multiply connected' for such configurations. Our task will be to evaluate the irreducible constants for different lattices, and to show how to express all other lattice constants in terms of them.

Fig. 5



Spin counts. Typical low-temperature configurations arising from four points ($p=4$).

5.1.2. Low temperature configurations

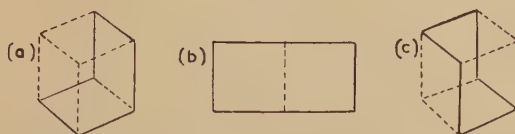
Series expansions at low temperatures are generally more difficult to derive or use than at high temperatures. For the Ising model the form of the expansions has been discussed in § 3.6.1 and the topological problem is one of 'spin counts', i.e. of classifying and enumerating the configurations arising from a set of p points of the lattice (fig. 5). We can define lattice constants per site as before, but we now use capital letters (e.g. P_{5a}) to distinguish them from high-temperature lattice constants. We still find it convenient to classify low-temperature configurations by the number of lines which they contain. The two sets of lattice constants are related, but the relations are not always simple to derive. Thus P_4 is the set of all quadrilaterals none of whose opposite corners are nearest neighbours; P_4 is contained within p_4 , but its complete determination will also involve p_{5a} and p_{6d} . In general the line count of a given linear graph is therefore larger than the corresponding spin count. It will again be our task to show how to calculate low-temperature constants for various lattices.

5.2. High-temperature Lattice Constants

5.2.1. The method of space types

The first few lattice constants can readily be determined for all lattices by elementary geometry. Let us consider, for example, simple closed polygons on the simple cubic lattice. The first non-zero closed polygon is the quadrilateral, and it is clear that this lattice admits only of quadrilaterals that are plane squares. Through each site of the lattice there pass twelve squares, four in each coordinate plane. The number of distinct squares for a lattice of N points is thus $3N$; hence for this lattice $p_4=3$. When we come to examine the number of hexagons we find that there are three possible space types (fig. 6), and that these can be placed on the lattice in $12N$, $6N$, $4N$ ways respectively; hence $p_6=22$.

Fig. 6



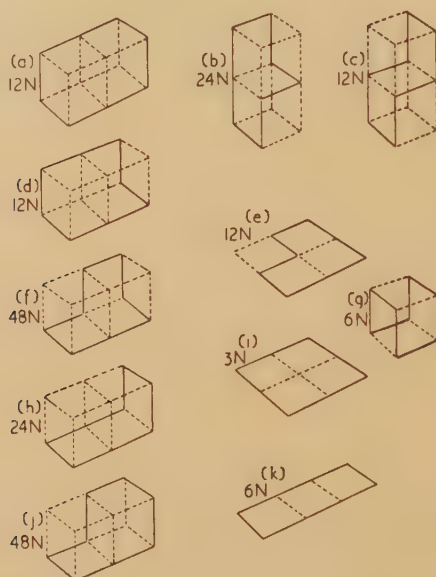
Hexagons on the simple cubic lattice. (a) $12N$, each pair of opposite edges determines two configurations; (b) $6N$, there are two independent polygons in each coordinate plane; (c) $4N$, each pair of opposite vertices determines one configuration.

It is clear that great care and effort is necessary to obtain higher terms. The method of procedure was completely systematized by Wakefield (1952); to obtain any new term all the space types derived in previous terms must be expanded in all possible ways to include the extra bonds, and the new space types must be classified for symmetry. In fig. 7 we have further illustrated the method by listing the 11 types of octagon for the simple cubic lattice, and from this we deduce that $p_8=207$. However, the number of space types increases rapidly, and there are 73 types of decagon, and 756 types of dodecagon. It is not surprising that Wakefield's calculation of the latter contained slight errors, but these have subsequently been corrected (Domb and Sykes 1957, Rushbrooke and Eve 1959); the correct values are $p_{10}=2412$, $p_{12}=31754$.

The classification of polygons on a lattice into various space types provides complete topological information regarding these polygons, and enables one to determine useful additional configurational data. For example from the hexagons in fig. 6 we can deduce that $p_{7a}=18$, and for low-temperature configurations $P_6=4$, $P_{7a}=18$. However, it is difficult to ensure that no space types have been overlooked at each stage, and the determination of the symmetry properties of any space type is not at all simple. Also for a lattice like the face-centred cubic the method is very cumbersome, and the polygons are much more difficult to visualize and draw.

We shall therefore describe an alternative method of counting polygons, which can be used as an independent approach to the problem, or as a check on the enumeration of space types. However, we must emphasize that the classification of the first few polygons on a lattice into space types is of great use; for evaluating certain types of irreducible constant the space-type technique is the only one which has so far proved applicable (§ 5.2.5).

Fig. 7



Octagons on the simple cubic lattice (after Wakefield). (11 types, total contribution $207N$, $p_8=207$.)

5.2.2. Use of the random walk problem. Path factors

Let us consider random walks on a given lattice starting at any point of the lattice, and returning to the starting point after l steps. We can characterize each walk graphically by means of the configuration which the walker describes; thus for the simple cubic lattice the first possible return occurs after two steps by reversing the direction of the initial step, and this can be represented by — . After four steps there are three possibilities which can be represented by



(A heavy line is described in both directions during the walk; a weak line

is described in only one direction). Hence the total number of such random walks, r_l , can be split up into contributions from various configurations, and we can write for this lattice

$$r_2 = 6 = 2 \left[\begin{array}{c} \text{—} \\ (3) \end{array} \right]$$

$$r_4 = 90 = 2 \left[\begin{array}{c} \text{= =} \\ (3) \end{array} \right] + 4 \left[\begin{array}{c} \text{^} \\ (15) \end{array} \right] + 8 \left[\begin{array}{c} \square \\ (3) \end{array} \right]. \quad (1)$$

The numbers in brackets under each configuration represent the values of the corresponding lattice constants. The numbers before the square brackets represent the number of ways in which the configuration can be described by a random walker who returns to his starting place after l steps. To evaluate this combinatorial factor for a given configuration we must sum the number of returns over all vertices of the configuration, since any such vertex can be the lattice point from which the walk starts. The combinatorial factor is a property of the configuration, and does not depend on the lattice considered.

Expansions such as (1) are useful for calculating properties of matrices associated with crystal lattices; for example they have been used in connection with the vibration spectra of disordered crystals (Domb *et al.* 1959). Explicit formulae can be derived for many of the combinatorial factors (some results are given in Appendix I), and r_l can readily be found by the use of generating functions (Appendix II). Hence relations such as (1) can be used as a check on the evaluation of the lattice constants.

For higher terms where the number of component configurations increases rapidly it is convenient to enumerate only silhouettes of a given configuration, and not differentiate between the number of times any line is

traversed. Thus in r_3 the silhouette $\left[\begin{array}{c} \text{^} \end{array} \right]$

will correspond to terms

$$\left[\begin{array}{c} \text{= =} \text{—} \end{array} \right] \text{ and } \left[\begin{array}{c} \text{= =} \end{array} \right]$$

in our previous notation; and $\left[\begin{array}{c} \square \end{array} \right]$

corresponds to $\left[\begin{array}{c} \square \\ \square \end{array} \right], \left[\begin{array}{c} \text{= =} \\ \square \end{array} \right], \left[\begin{array}{c} \text{=} \text{—} \\ \square \end{array} \right], \left[\begin{array}{c} \text{= =} \\ \text{= =} \end{array} \right]$

Appendix I contains the analysis in this notation, of r_2 , r_4 , r_6 and r_8 for the simple quadratic and simple cubic lattices. The coefficients outside the silhouettes will now be referred to as *path factors*. A *path factor* of order l for a given configuration is thus the total number of returns to the origin in a random walk of l steps on the configuration which traverses each line of the configuration at least once; this number is to be summed taking each vertex of the configuration in turn as origin.

We have extended the analysis of Appendix I to r_{10} for the simple quadratic, simple cubic and body-centred cubic lattices but since some 50 configurations are involved we have not reproduced the results here. In fact, although this analysis is of importance for matrix problems connected with crystal lattices, it is somewhat cumbersome as a check of lattice constants because of the large number of configurations which enter. We shall now proceed to a method in which all configurations which are not closed can be removed.

5.2.3. *Elimination of immediate reversals*

The problem of a random walk on a lattice in which no immediate reversals are allowed has been considered by several authors [(Gillis (1955), Temperley (1956), Domb and Fisher (1958))]; in such a walk two successive

steps \Rightarrow cannot occur, although steps like  can occur.

Domb and Fisher gave a simple formula relating q_l , the number of returns to the origin in a no-reversal walk on a regular lattice, to r_l the number of returns in a standard walk:

$$q_l = \frac{(\sigma-1)}{2} [(1)^l + (-1)^l] + r_l - \sigma l r_{l-2} + \sigma^2 \frac{l(l-3)}{2!} r_{l-4} - \sigma^3 \frac{l(l-4)(l-5)}{3!} r_{l-6} + \dots (\sigma=q-1). \quad (2)$$

This formula applies to walks in which 'improper closures' are excluded, i.e. walks which start and end in opposite directions, e.g.



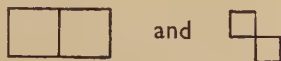
From eqn. (2) values of q_l can readily be calculated from r_l , and some results are tabulated in Appendix II; for the simple cubic lattice $q_2=0$, $q_4=24$, $q_6=264$, $q_8=4584$.

If we now analyse the q_l into contributions from various configurations in the same manner as r_l in Appendix I, only closed configurations can enter into the analysis, and this leads to a substantial simplification.

Thus for q_4 and q_6 only simple closed polygons enter, and we may write

$$\left. \begin{aligned} q_4 &= 24 = 8 \left[\begin{array}{|c|} \hline \square \\ \hline \end{array} \right] & (3) \\ q_6 &= 264 = 12 \left[\begin{array}{|c|} \hline \text{hexagon} \\ \hline \end{array} \right] & (22) \end{aligned} \right\} \dots \dots \dots (3)$$

Hence we have verified the result of § 5.2.1 that $p_6=22$ without any geometrical considerations. When we come to consider q_8 two more closed configurations enter our analysis



We shall denote each configuration by the corresponding lattice constant symbol. (See table A, Appendix III), and for q_8 we may write

$$q_8 = \lambda_8(8)p_8 + \lambda_{7a}(8)p_{7a} + \lambda_{8h}(8)p_{8h} + \lambda_4(8)p_4. \quad \dots \dots (4)$$

Here the λ 's may again be referred to as *path factors* but they differ from the corresponding path factors of § 5.2.2 for they represent the number of returns to the origin summed over all vertices in a random walk with no immediate reversals (and no improper closures); again each line of the configuration must be described at least once in the walk. Quite generally we may write

$$q_l = \sum_{x; s \leq l} \lambda_{sx}(l)p_{sx}, \quad \dots \dots \dots (5)$$

where the variable l in the λ 's tells us that the walk consists of l steps.

It is clear that $\lambda_8(8)=16$, $\lambda_4(8)=8$ (successive squares must be described in the same sense since immediate reversals are not allowed). $\lambda_{7a}(8)$ is a little more tricky. From fig. 8 it will be seen that starting from the vertices A, C, D, F the configuration can be described in two ways (arrows as shown or completely reversed); starting from B, E it can be described in four ways; hence $\lambda_{7a}(8)=16$. Similarly P_{8h} can be described in four ways starting from A, B, C, D, E, F (fig. 9 arrows as shown or completely reversed), and in eight ways starting from G (an additional factor 2 arising from the initial choice of squares); hence $\lambda_{8h}(8)=32$. Thus we have the relation

$$q_8 = 4584 = 16p_8 + 32p_{8h} + 16p_{7a} + 8p_4, \quad \dots \dots (6)$$

and this can be used as a check on the values of p_8 , p_{7a} , p_{8h} . But in fact p_{7a} and p_{8h} are reducible configurations, and we shall show in the next section how they can be expressed in terms of p_4 ; eqn. (6) can then be used as a means of evaluating p_8 .

The analysis of q_l is particularly useful for the face-centred cubic lattice in which polygons occur with odd and even numbers of sides, and configurations are difficult to visualize geometrically. We have for this lattice $q_2=0$, $q_3=48$, $q_4=264$, $q_5=1680$, $q_6=17016$.

We can immediately deduce p_3 , p_4 and p_5 from

$$\left. \begin{aligned} q_3 &= 48 = 6p_3, \\ q_4 &= 264 = 8p_4, \\ q_5 &= 1680 = 10p_5, \end{aligned} \right\} \dots \dots \dots (7)$$

and by analogy with (6) we find

$$q_6 = 17016 = 12p_6 + 24p_{6c} + 12p_{5a} + 6p_3. \dots \dots \dots (8)$$

Fig. 8

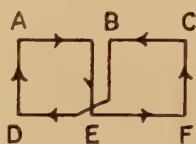
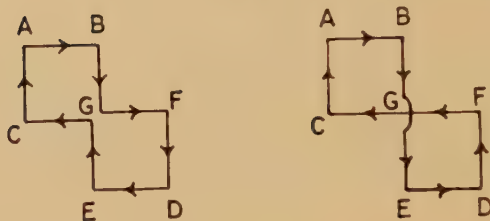


Fig. 9



When we extend the analysis of q_l to higher terms we find that substantial numbers of other lattice constants enter into relations such as (6) and (8), and the determination of the path factors becomes quite involved. We will therefore now consider methods of evaluating other lattice constants, reducible and irreducible, and alternative sources of information regarding path factors.

5.2.4. Reducible constants

By *reducible configurations* we mean configurations which can be constructed by placing together two lower order configurations at one vertex or along one side; in a terminology analogous to that of §5.1 we may say that reducible configurations are made up of trees with cutting points or stars with cutting lines. For example p_{6c} is formed from two triangles with a vertex in common, and p_{5a} from two triangles with a side in common.

The method of calculation of such constants is best illustrated by examples, and we shall first calculate p_{6c} and p_{5a} in terms of lower order constants. We first note that since there are Np_l simple l -sided polygons

on the lattice, and each polygon has l vertices, lp_l such polygons pass through any point of the lattice (e.g. four squares pass through each point of the simple quadratic lattice). Similarly since there are $Nq/2$ bonds in the lattice, and each polygon has l sides, $2lp_l/q$ polygons pass through any bond of the lattice (e.g. two squares pass through each bond of the simple quadratic lattice).

We now consider two independent sets of triangles passing through any point of the lattice, and we form configurations by pairing together one triangle of each set. There will thus be a total of $(3p_3)^2$ configurations for each point of the lattice; among these configurations each p_{6c} will be described twice (because of the symmetry with respect to constituent triangles); each p_{5a} will be described four times, twice from each of the vertices at the end of the diagonal; and each p_3 will be described three times, once from each vertex. Hence we may write

$$9p_3^2 = 2p_{6c} + 4p_{5a} + 3p_3. \quad \dots \dots \dots (9)$$

We next consider two independent sets of triangles passing through every bond of the lattice, and pair together triangles as before. There are now $(6p_3/q)^2$ configurations through each link, and hence the total number of configurations in the lattice is $(Nq/2)(6p_3/q)^2 = 18Np_3^2/q$. We shall form p_{5a} twice because of the symmetry with respect to constituent triangles, and p_3 three times once from each side. Hence we have

$$18p_3^2/q = 2p_{5a} + 3p_3. \quad \dots \dots \dots (10)$$

From (9) and (10) we deduce that

$$\left. \begin{aligned} p_{5a} &= \frac{9p_3^2}{q} - \frac{3p_3}{2}, \\ p_{6c} &= \left(\frac{9}{2} - \frac{18}{q} \right) p_3^2 + \frac{3p_3}{2}. \end{aligned} \right\} \dots \dots \dots (11)$$

We can proceed in a similar manner to determine p_{7a} , p_{8h} for the simple quadratic and simple cubic lattices. When two squares are placed together with a vertex or side in common on these lattices the only configurations formed are p_{7a} , p_{8h} or p_4 , and we can deduce by analogy with (11) that

$$\left. \begin{aligned} p_{7a} &= \frac{16p_4^2}{q} - 2p_4, \\ p_{8h} &= \left(8 - \frac{32}{q} \right) p_4^2 + 2p_4. \end{aligned} \right\} \dots \dots \dots (12)$$

However, for the body-centred cubic lattice other configurations can be formed; if the quadrilaterals have opposite vertices in common p_{8r} will be formed, and if they have two adjacent sides in common p_{6a} will be formed. Both of these are irreducible constants, and we must evaluate them before we can determine p_{7a} and p_{8h} . If we put together two independent sets of quadrilaterals passing through a lattice point, p_{8h} will be formed twice, p_{7a} four times and p_4 four times as before; but in addition p_{8r} will be formed 12 times (6 independent quadrilaterals can be chosen from the

pairs of double bonds connecting opposite vertices, and a factor 2 arises as in p_{7a} because of the two vertices), and p_{6a} will be formed 18 times (6 times from each of the vertices at the end of the diagonal and twice from each of the other vertices). Hence the appropriate relation is

$$16p_4^2 = 2p_{8b} + 4p_{7a} + 4p_4 + 12p_{8r} + 18p_{6a}. \quad (13)$$

Putting together two sets of quadrilaterals passing through a bond of the lattice we will form p_{7a} twice and p_4 four times as before, and p_{6a} twelve times (twice from each of the 6 lines of the configuration). Hence

$$32p_4^2/q = 2p_{7a} + 4p_4 + 12p_{6a}. \quad (14)$$

For the face-centred cubic lattice configurations containing triangles enter, and p_{6d} , p_{7c} must also be included. In the same manner as before we can show that to (13) and (14) we must add respectively

$$4p_{8s} + 6p_{7c} + 24p_{6d}, \quad (15)$$

$$2p_{7c} + 12p_{6d}.$$

Using eqn. (11) and substituting in (7) and (8) we can express p_6 in terms of the q_i ,

$$12p_6 = q_6 - 4q_3 - 3q_3^2(1 - 3/q). \quad (16)$$

The analysis of q_7 corresponding to (8) is

$$q_7 = 14p_7 + 28p_{7e} + 84p_{7g} + 14p_{6b} + 28p_{5a}. \quad (17)$$

No irreducible constants arise, and proceeding as before we can derive the formula

$$14p_7 = q_7 + 7q_3\left(\frac{q_3}{q} - 1\right)\left(\frac{q_3}{q} - 3\right) - 7q_3q_4(1 - 3/q). \quad (18)$$

Equations (16) and (17) are valid for all regular lattices but are most useful for close-packed lattices. When we come to the general expression for p_8 ((6) is valid only for the simple quadratic and simple cubic lattices) we must introduce irreducible constants as in (13), and we shall therefore now consider how these can be evaluated.

5.2.5. Irreducible constants

Any lattice constants which cannot be expressed in terms of lower-order constants we refer to as irreducible. The most important class of irreducible configurations are the simple polygons. After this the most frequently occurring class are configurations involving a double bridge, such as p_{6a} , p_{7f} , p_{8c} (Appendix III, table A). These can be determined by the method of space types, e.g. from fig. 6 we can deduce that $p_{8c} = 24$ for the simple cubic lattice (note that double bridges arising from (c) are merely a repetition of those from (a)). But we shall now show that they can be calculated from the properties of random walks on the lattice and for three dimensional lattices this method is usually to be preferred.

Let $\phi(x, y, z)$ denote the generating function for random walks on the lattice. Values of ϕ for various simple lattices are given in Appendix II. For the face-centred cubic lattice, for example,

$$\phi = (y^{-1} + y)(z^{-1} + z) + (z^{-1} + z)(x^{-1} + x) + (x^{-1} + x)(y^{-1} + y), \quad (19)$$

and this can be written symbolically

$$\phi = \sum xy, \quad (20)$$

where the sum is taken over all points which are equivalent under the symmetry operations of the lattice (permutations of x, y, z , and inversions $x \rightarrow x^{-1}, y \rightarrow y^{-1}, z \rightarrow z^{-1}$). From the terms in ϕ^l we can determine $R_l(a, b, c)$, the number of walks which arrive at the lattice point (a, b, c) after l steps. As before, we can eliminate all walks with immediate reversals; Domb and Fisher (1958) derived the generating function for such walks, and from their results the following expression analogous to (2) can be deduced for $Q_l(a, b, c)$ after l steps:

$$Q_l(a, b, c) = R_l - [\sigma(l-1) + 1]R_{l-2} + \frac{(l-3)}{2!}[\sigma(l-2) + 2]\sigma R_{l-4} - \dots \quad (21)$$

For the face-centred cubic we find that

$$\left. \begin{aligned} \phi^2 &= 12 + 4\sum xy + 4\sum x^2 + 2\sum x^2yz + \sum x^2y^2, \\ \phi^3 &= 48 + 45\sum xy + 24\sum x^2 + 12\sum x^2y^2 + 18\sum x^2yz \\ &\quad + 9\sum x^3y + 3\sum x^3y^2z + 6\sum x^2y^2z^2 + \sum x^3y^3. \end{aligned} \right\} \quad (22)$$

Applying (21) we derive the corresponding polynomials for no-reversal walks:

$$\left. \begin{aligned} \psi_2 &= 4\sum xy + 4\sum x^2 + 2\sum x^2yz + \sum x^2y^2, \\ \psi_3 &= 48 + 22\sum xy + 24\sum x^2 + 12\sum x^2y^2 + 18\sum x^2yz \\ &\quad + 9\sum x^3y + 3\sum x^3y^2z + 6\sum x^2y^2z^2 + \sum x^3y^3. \end{aligned} \right\} \quad (23)$$

From (23) let us now form the quantity $\sum Q_2(Q_2-1)/2!$, where the summation is taken over all points except the origin. Since $\sum xy$ represents 12 equivalent points, $\sum x^2$ 6 points, $\sum x^2yz$ 24 points and $\sum x^2y^2$ 12 points, this sum is equal to

$$\frac{1}{2}[4 \cdot 3 \cdot 12 + 4 \cdot 3 \cdot 6 + 2 \cdot 1 \cdot 24 + 1 \cdot 0 \cdot 12] = 132. \quad (24)$$

This number represents the number of pairs of two-step bridges we can select from the origin to the ensemble of accessible points. From the form of the sum it is clear that the bridges are all distinct and can only form a quadrilateral. On summing over all points of the lattice as origin, and dividing by N we shall form each quadrilateral four times (once from each vertex as origin); hence $4p_4 = 132$, $p_4 = 33$. Thus we have confirmed the value of p_4 derived in §5.2.3.

If we now form $\sum Q_2(Q_2-1)(Q_2-2)/3!$ we will enumerate all groups of three two-step bridges from the origin to the set of accessible points.

Summing as before we will describe each p_{6a} twice; we thus find that for the face-centred cubic $p_{6a}=36$. Similarly, if we form

$$\sum Q_2(Q_2-1)(Q_2-2)(Q_2-3)/4!$$

we can deduce that for this lattice $p_{8r}=9$.

When we consider configurations involving bridges of more than two steps (e.g. p_{7f}) we must allow for the possibility of some steps in the bridges being identical. Thus if we form $\sum Q_3Q_2$ we will not only describe pentagons but also the open configurations



the latter will be described 4 times, twice from A, and once each from B, C. Hence

$$\sum Q_3Q_2=10p_5+4 \left[\text{---} \triangle \right] \quad . \quad . \quad . \quad . \quad (25)$$

and this can be used as a check on the constants which have been determined by other means.

Similarly we may derive the relation

$$\sum Q_3Q_2(Q_2-1)/2!=2p_{7f}+4p_{6b}+4p_{5a}, \quad . \quad . \quad . \quad . \quad (26)$$

and from it we deduce that $p_{7f}=600$ (face-centred cubic).

No general recipe can be given for calculating all irreducible constants; many of those not amenable to the methods described so far correspond to tightly bound configurations and can readily be found by inspection of space types on the lattice (e.g. for the face-centred cubic $p_{6a}=2$). Others can be found by more detailed examination of the bridges enumerated by (23). Thus to calculate p_{7h} for the face-centred cubic we can examine all two-step bridges, and determine how many pairs are nearest neighbours after the first step; it will be found that of the four bridges from the origin to $\sum xy$ there are two such pairs, and of the four bridges from the origin to $\sum x^2$ there are four such pairs. We therefore deduce that

$$2p_{7h}=12.2.2+6.4.2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and hence that $p_{7h}=48$.

The remaining irreducible constants p_{8c} , p_{8d} given in Appendix III, table A can be determined from the relations

$$\left. \begin{aligned} \sum Q_2Q_3(Q_3-1)/2! &= 2p_{8d} + 2p_{8f} + 4p_{7b} + 4p_{7c} + 4p_{7f} + 2p_{7h} \\ &\quad + 8p_{6c} + 4p_{6b} + 4p_{5a} + 2 \left[\text{---} \diamond \text{---} \right], \\ \sum Q_4Q_2(Q_2-1)/2! &= 2p_{8c} + 2p_{8f} + 4p_{8l} + 8p_{7a} + 12p_{7c} + 6p_{7g} \\ &\quad + 48p_{6d} + 12p_{6a} + 4p_{5a}. \end{aligned} \right\} \quad . \quad (28)$$

The coefficients in these relations become quite complex, and are similar

to path factors, but are easier to determine directly because of the absence of 'improper closures'. To evaluate the second line in (28) for the face-centred cubic we require the next term of (23) which is

$$\begin{aligned}\psi_4 = & 264 \sum xy + 152 \sum x^2 + 136 \sum x^2 yz + 114 \sum x^2 y^2 \\ & + 96 \sum x^3 y + 36 \sum x^4 + 72 \sum x^2 y^2 z^2 + 52 \sum x^3 y^2 z + 24 \sum x^3 y^3 \\ & + 24 \sum x^4 yz + 16 \sum x^4 y^2 + 12 \sum x^3 y^3 z^2 + 6 \sum x^4 y^2 z^2 \\ & + 4 \sum x^4 y^3 z + \sum x^4 y^4. \quad (29)\end{aligned}$$

Having shown how to evaluate irreducible constants we can now return to the extension of (18). For p_8 we have derived the formula

$$\begin{aligned}16[p_8 + 3p_{6a} - 6p_{8r} - 33p_{6d}] = & q_8 - 5q_4 - 80q_3 - 4(2q_5q_3 + q_4^2)(1 - 3/q) \\ & - 32q_4q_3/q + q_3^2 \left(\frac{128}{q} + 16 - 4q \right) + 8q_3^2(3q_4 - 8q_3)/q^2. \quad (30)\end{aligned}$$

We have also obtained an expression for p_9 , but this involves the irreducible constant p_{9h} , which can be calculated from the relation

$$\sum Q_3 Q_2 (Q_2 - 1)(Q_2 - 2)/3! = 2p_{9h} + 2p_{8p} + 4p_{7h}. \quad . . . (31)$$

We then find

$$\begin{aligned}18[p_9 - 6p_{9h} + 2p_{7f} - 10p_{7h} + 72p_{6a}p_3/q + 8p_{6d}(26 - 99p_3)] \\ = q_9 + 200q_3 - 9(q_6q_3 + q_5q_4)(1 - 3/q) - 36q_5q_3/q + q_4q_3 \left(\frac{81}{q} + 36 - 9q \right) \\ - 522q_3^2/q + 27q_5q_3^2/q^2 + 27q_4^2q_3/q^2 - 144q_4q_3^2/q^2 \\ + q_3^3 \left(\frac{462}{q^2} - \frac{81}{q} + 15 \right) - 48q_3^4/q^3. \quad (32)\end{aligned}$$

The determination of path factors for expressions like (30) and (32) is most intricate, and hence their verification is of considerable importance; methods which have been used for this purpose will be described in detail in §5.2.9.

Relations like (30) and (32) are topological, and can be applied equally well to all regular lattices. We have illustrated their use by application to the face-centred cubic lattice since this is the lattice for which the algebraic technique is the most powerful, and the space type method the most difficult. For example we find that $p_9 = 301, 376$, and this certainly corresponds to more than 6000, and probably to more than 10 000, distinct space types.

For loose-packed lattices only even terms occur, and many of the terms in expressions like (30) are zero. We can give a general formula for p_{10} as follows:

$$\begin{aligned}20[p_{10} - 6p_{10c} + 2p_{8c} + 2p_{8t} - 12p_{6a}(4 - q_4/q)] \\ = q_{10} - 10q_4q_6(1 - 3/q) - 5q_4^2(q - 2)(1 - 2/q) \\ + 10q_4(1 - q_4/q)(4 - q_4/q). \quad (33)\end{aligned}$$

The values of the lattice constants discussed in the foregoing sections corresponding to closed configurations are listed in Appendix III, table A for a number of simple lattices.

5.2.6. Open configurations

In contrast to closed configurations, *open configurations* have at least one vertex to which only one line is attached. Open configurations are all reducible since we can always reduce the single vertex; they are very numerous and we have therefore not used a symbol for them but represent the corresponding lattice constants by a diagram, e.g.

$$[\text{Y}], [\text{A}], [\text{X}].$$

The method of calculation of open configurations is closely similar to §5.2.4, and we shall illustrate it by the example of

$$[\square] .$$

We can attach a single bond to every p_4 in $4(\sigma-1)$ ways; if the second end of the bond remains free we form

$$[\square] ;$$

but if it is the opposite vertex of the quadrilateral we form p_{5a} , and when we sum over all lattice points we will describe each p_{5a} twice, once from each end of the diagonal. Thus

$$4(\sigma-1)p_4 = [\square] + 2p_{5a} \quad . \quad . \quad . \quad . \quad (34)$$

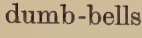
A class of open configurations of particular interest in the theory of polymer solutions is that of simple chains with l bonds, the lattice constant of which we denote by c_l . A general theorem has been enunciated by Sykes which enables c_l to be expressed in terms of lattice constants of closed configurations, and greatly simplifies the counting problem. A detailed proof of this theorem will be available elsewhere (Sykes 1960), and we shall therefore only indicate the line of approach.

Let us add another bond to c_l ; this can be done in $2\sigma c_l$ ways, one from each end. We form c_{l+1} twice and other configurations which are either polygons or 'tadpoles' (fig. 10a). If we now add another bond to the free end of a tadpole, we form either tadpoles or closed configurations which are 'dumb-bells', 'orthodox figure eights', or 'star figure eights' (fig. 10b, c, d). If we take careful account of the number of times

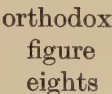
the various configurations are formed, we can derive the following relation:

$$c_{l+1} - 2\sigma c_l + \sigma^2 c_{l-1} = lp_l - (l+1)p_{l+1} \\ + 4\sum \left[\text{---} \bigcirc \text{---} \bigcirc \text{---} \right] + 4\sum \left[\infty \right] + 6\sum \left[\text{---} \bigcirc \text{---} \right] . \quad (35)$$

dumb-bells



orthodox
figure
eights



star
figure
eights


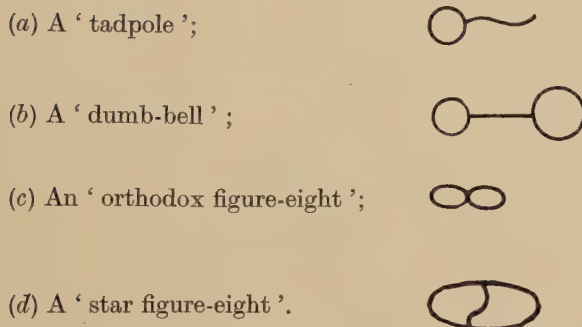


Fig. 10



The sums in the last three terms on the right-hand side must be taken over all configurations of the appropriate type formed from $(l+1)$ lines.

It will be seen that using (35) the data given in Appendix III, table A enable us immediately to write down the first eight chains for the face-centred cubic lattice :

$$\left. \begin{aligned} c_1 &= 6, \\ c_2 &= 66, \\ c_3 &= 22c_2 - 121c_1 - 3p_3 = 702, \\ c_4 &= 22c_3 - 121c_2 + 3p_3 - 4p_4 = 7350, \\ c_5 &= 22c_4 - 121c_3 + 4p_4 - 5p_5 + 6p_{5a} = 76266, \\ c_6 &= 22c_5 - 121c_4 + 5p_5 - 6p_6 + 4p_{6c} + 6(p_{6a} + p_{6b}) = 786858 \\ c_7 &= 22c_6 - 121c_5 + 6p_6 - 7p_7 + 4p_{7d} + 4p_{7e} + \\ &\quad + 6(p_{7a} + p_{7b} + p_{7f}) = 8086074, \\ c_8 &= 22c_7 - 121c_6 + 7p_7 - 8p_8 + 4(p_{8j} + p_{8k}) + 4(p_{8g} + p_{8h}) \\ &\quad + 6(p_{8a} + p_{8b} + p_{8c} + p_{8d}) = 82848522. \end{aligned} \right\} . \quad (36)$$

For other lattices the chain series can be pushed considerably further ; in two dimensions special methods are available (§ 5.4.4) and for the simple quadratic lattice as many as 18 terms have been evaluated. The numerical results derived so far for a number of lattices have been tabulated by

Fisher and Sykes (1959), and are reproduced in Appendix III, table B (the difference of a factor 2 arises since Fisher and Sykes consider non-self-intersecting walks starting from the origin whereas we consider configurations.) Numerical values of lattice constants for open configurations of up to six lines are also tabulated in this Appendix.

5.2.7. Separated configurations

In the Mayer Theory separated configurations are eliminated at a very early stage. However, in configuration problems on crystal lattices they present a more difficult problem, and can be calculated by a method similar to that of § 5.2.4 for reducible configurations. Let us, for example, calculate the lattice constant corresponding to two separated triangles, which we denote by $[p_3, p_3]$ (the definition being *per lattice point* as before). Consider all configurations which will be formed by pairing together triangles from two independent sets of all the Np_3 triangles of the lattice. Each p_{5a} will be formed twice, when the triangles have a side in common, each p_{6c} twice when they have a vertex in common, and each p_3 once when they coincide; the remaining configurations will all belong to $[p_3, p_3]$ and will be described twice, by symmetry. Hence

$$\begin{aligned} (Np_3)^2 &= 2Np_{5a} + 2Np_{6c} + Np_3 + 2N[p_3, p_3], \\ \text{or } [p_3, p_3] &= \frac{1}{2}Np_3^2 - p_{5a} - p_{6c} - p_3/2. \end{aligned} \quad (37)$$

To determine $[p_3, p_3, p_3]$ we must consider all configurations which can be formed by one each of three independent sets of all the Np_3 triangles of the lattice. Proceeding as before we find that

$$\begin{aligned} (1/N)(Np_3)^3 &= 6[p_{5a}, p_3] + 6[p_{6c}, p_3] + 6[p_3, p_3] + 6[p_3, p_3, p_3] \\ &\quad + 6p_{9c} + 6p_{9d} + 6p_{9g} + 6p_{8l} + 6p_{8m} + 6p_{8q} + 6p_{7c} + 6p_{7g} \\ &\quad + 6p_{6c} + 24p_{6d} + 6p_{5a} + p_3. \end{aligned} \quad (38)$$

The terms in (38), although lengthy, are not difficult to derive; we look through table A, Appendix III, and pick out all configurations which can be completely described by three triangles. We must now reduce $[p_{5a}, p_3]$ and $[p_{6c}, p_3]$ as in (37):

$$\begin{aligned} Np_{5a}p_3 &= [p_{5a}, p_3] + p_{8l} + p_{8m} + p_{8q} + 2p_{7c} + 3p_{7g} + 12p_{6d} + 2p_{5a}, \\ Np_{6c}p_3 &= [p_{6c}, p_3] + 2p_{9c} + 3p_{9d} + 3p_{9g} + 2p_{8l} + p_{8m} + 2p_{8q} + p_{7c} + 2p_{6c}. \end{aligned} \quad (39)$$

Hence we obtain

$$\begin{aligned} [p_3, p_3, p_3] &= \frac{1}{6}N^2p_3^3 - N[p_{6c}p_3 + p_{5a}p_3 + p_3^2/2] \\ &\quad + [p_{9c} + 2p_{9d} + 2p_{9g} + 2p_{8l} + p_{8m} + 2p_{8q} + 2p_{7c} + 2p_{7g} + 2p_{6c} + 8p_{6d} \\ &\quad + 2p_{5a} + p_3/3]. \end{aligned} \quad (40)$$

This formula can also be checked by the use of finite clusters of points, as will be shown in § 5.2.9.

Formulae for separated configurations needed for the no-field series for the Ising model ($s = \frac{1}{2}$) are given in Appendix III, table C; they suffice to determine nine terms for close-packed lattices and ten terms for loose-packed lattices.

The same technique can be used for evaluating lattice constants for separated open configurations. However, they are more numerous, and we shall not reproduce any details of the calculations. For the Ising model with $s = \frac{1}{2}$ open configurations can be eliminated in many problems of practical interest. However, for general s and for the Heisenberg model these configurations always arise in the counting problems, and we have therefore tabulated the terms corresponding to five lines or less in Appendix III, table C. We have given the numerical value of the coefficient independent of N in an expression like the right-hand side of (40), since this is the value required for the appropriate term of the free energy expansion (§3.6.1, §5.2.10). (The numerical values are multiplied by $l!$ to avoid fractions.)

5.2.8. Homogeneous non-regular lattices

We shall now consider the extension of the methods developed above to lattices in which points are all equivalent but bonds are not all equivalent. We have come across a two-dimensional example of such a lattice in fig. 36, §3. The most important lattice of this kind is the hexagonal close-packed; the bonds may be divided into two separate groups of six, those lying in a plane of close packing, and those connecting two successive layers of close-packing.

Most of the formulae and methods described previously do not use bond-equivalence, and retain their validity. In this category are (2) (a detailed justification will be given in §5.2.9), (7), (8), (9), (17), (25), (26), (28), (31), (35), (37) and (40). In fact the only feature using bond equivalence is the reduction in §5.2.4 of a configuration with a cutting line; hence an equation like (10) remains valid only if the numbers of triangles passing through each type of bond is the same.

The generation of walks on non-Bravais lattices is not as simple as on Bravais lattices, and needs slightly more general treatment. Lattice points which constitute the unit cell must be considered separately from those within the unit cell, and instead of a simple generating function like (19), we are led to the traces of the n th powers of matrices whose order is equal the number of points in a unit cell. For the hexagonal close-packed the matrix is 2×2 , since we must differentiate between odd and even numbered close-packed layers. We may write for the position after l steps

$$\chi_l = T^l + {}^1C_1 T^{l-1}(z+z^{-1})U + {}^1C_2 T^{l-2}(z+z^{-1})^2UV \\ + {}^1C_3 T^{l-3}(z+z^{-1})^3U^2V + \dots \quad (41)$$

Here T is the generating function in a close-packed plane, (i.e. of the triangular lattice),

$$T = x + x^{-1} + y + y^{-1} + xy^{-1} + x^{-1}y, \quad (42)$$

and z is the direction perpendicular to this plane; U represents a jump from a close packed layer to an adjacent close packed layer, and V the reverse jump,

$$\left. \begin{aligned} U &= x^{2/3}y^{1/2}(1+x^{-1}+y^{-1}), \\ V &= x^{-2/3}y^{-1/2}(1+x+y), \\ UV &= 3+T. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (43)$$

Domb and Sykes (1957c) noted that the number of returns to the origin in a random walk of l steps was exactly the same for cubic and hexagonal close-packed lattices (Fisher and Sykes have both given independent proofs of this interesting result). Hence from (7) p_3 , p_4 and p_5 are the same for both lattices.

Because of the difficulty of reducing configurations with a cutting line the method of § 5.2.5. is the most useful for the hexagonal close-packed lattice, and it can also be applied equally well to reducible configurations like p_{5a} , p_{6b} . Owing to the lower symmetry of the hexagonal close-packed lattice the classification of equivalent points is more complicated (as is also the space-type classification).

From (41) we readily deduce that

$$\begin{aligned} \chi_1 &= (x+x^{-1}+y+y^{-1}+xy^{-1}+x^{-1}y) + x^{2/3}y^{1/2}(z+z^{-1})(1+x^{-1}+y^{-1}), \\ \chi_2 &= 12 + 4(x+x^{-1}+y+y^{-1}+xy^{-1}+x^{-1}y) \\ &\quad + 2(xy+x^{-1}y^{-1}+x^2y^{-1}+x^{-2}y+x^{-1}y^2+xy^{-2}) \\ &\quad + (x^2+x^{-2}+y^2+y^{-2}+x^2y^{-2}+x^{-2}y^2) \\ &\quad + x^{2/3}y^{1/2}(z+z^{-1})[4(1+x^{-1}+y^{-1}) \\ &\quad + 2(x+y+x^{-2}+y^{-2}+x^{-2}y+xy^{-2}) \\ &\quad + 4(xy^{-1}+x^{-1}y+x^{-1}y^{-1})] \\ &\quad + (z^{-2}+z^2)[3+(x+x^{-1}+y+y^{-1}+x^{-1}y+xy^{-1})]. \end{aligned} \quad . \quad . \quad . \quad . \quad (44)$$

Groups of equivalent points have been bracketed together; although the expressions are long they have simple geometrical interpretations, as will be seen by drawing them on the triangular lattice. Forming

$$\sum Q_1 Q_2 (Q_2 - 1) / 2!$$

we find that $p_{5a} = 36$, as for the face-centred cubic lattice. However, on forming $\sum Q_2 (Q_2 - 1) (Q_2 - 2) / 3!$ we obtain

$$2p_{6a} = 4.6 + 4.6 + 4.6 + 2 = 74. \quad . \quad . \quad . \quad . \quad (45)$$

Hence $p_{6a} = 37$ and differs from the value of 36 for the face-centred cubic; from $\sum Q_2 (Q_2 - 1) (Q_2 - 2) (Q_2 - 3) / 4!$ we find that $p_{8r} = 9$ as for the face-centred cubic.

We may proceed further as for the face-centred cubic lattice. In fact the general result can be established that the number of triangles, quadrilaterals, and pentagons passing through each type of bond is the same; hence the reductions of § 5.2.4 remain valid for the hexagonal close-packed lattice. We then find from (30) ($p_{6d} = 2$, as for the face-centred cubic

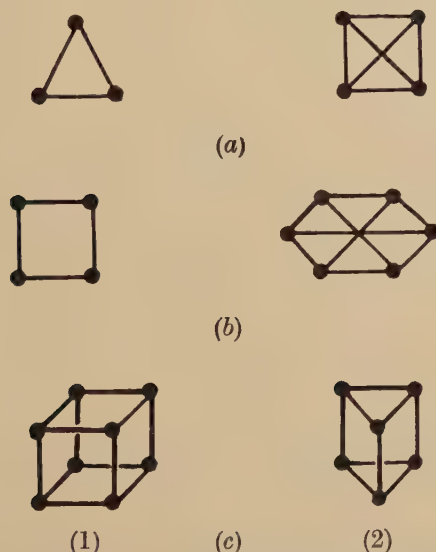
lattice) that $p_8 = 42066$. Similarly $p_{7h} = 51$ for the hexagonal close-packed lattice, and hence $p_9 = 301\,358$.

There are more 'tightly bound' configurations on the hexagonal close-packed than on the face-centred cubic, and in this sense it may perhaps be regarded as slightly more 'close-packed'.

5.2.9. The use of finite clusters of points

The configurational formulae derived so far in this chapter have in no way depended on lattice structure, and apply equally to finite clusters of points with connecting bonds. For such clusters the enumeration of configurational constants is often quite elementary, and hence they can be used as a check on topological formulae like (11) (17) or (40). We can readily extend our lattice classification to finite clusters. A cluster will

Fig. 11



Some finite clusters of points. (a) Close-packed clusters; (b) Loose-packed clusters; (c) Other homogeneous sets: (1) Cube, homogeneous and regular; (2) Prism, homogeneous and non-regular.

be described as *regular* if all points and bonds are equivalent, and *homogeneous* if all points (but not necessarily bonds) are equivalent. For finite clusters we shall use the term *configuration constant* instead of lattice constant, which we shall define *per site* as before. Thus, if the cluster consists of N points, it will contain Np_3 triangles, Np_4 quadrilaterals, etc.

We shall first make use of clusters with a high degree of symmetry. A *close-packed cluster* of N points is a set of N points every pair of which is connected by a bond. For four points this corresponds to a tetrahedron, as shown in fig. 11 *a*, and for six points to a hexagon with all diagonals

connected. A close-packed cluster of N points has coordination number $(N-1)$ which we denote by $(\sigma+1)$ in accord with our practice for standard lattices; we shall often refer to this cluster briefly as $CP(N)$.

We can also consider random walks on clusters, and can derive a formula for r_l the number of returns to the starting point after l steps. To do this we do not make use of generating functions, but instead establish a set of difference equations which can usually be solved quite easily. For a close-packed cluster the procedure is particularly simple, since all $(N-1)$ points other than the starting point 0 are equivalent. Denoting one of the equivalent points by P the difference equations are

$$\left. \begin{aligned} r_{l+1}(0) &= (\sigma+1)r_l(P), \\ r_{l+1}(P) &= r_l(0) + \sigma r_l(P). \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (46)$$

From this it is easy to show that $r_l(P)$ is the coefficient of x^{l-1} in the expansion of $[1 - \sigma x - (\sigma+1)x^2]^{-1}$ and hence that

$$r_l = \frac{\sigma+1}{\sigma+2} [(\sigma+1)^{l-1} + (-1)^l]. \quad . \quad . \quad . \quad . \quad (47)$$

Domb and Sykes (1957 a) observed that the formulae (2) for q_l remained valid for homogeneous clusters of points. The argument given by Domb and Fisher (1958), which is based on the use of generating functions, is no longer valid in this case, but the following alternative derivation, due to Fisher, provides a clear insight into the essential topological nature of the formula. We can rearrange (2) so as to give r_l in terms of q_l as follows:

$$r_l = q_l + \sigma l q_{l-2} + \sigma^2 \frac{l(l-1)}{2!} q_{l-4} + \dots + B_l(\sigma) \quad . \quad . \quad . \quad (48)$$

where the q_l series terminates at q_3 if l is odd, and at q_2 if l is even. Each term then has a simple topological interpretation, the totality of random walk returns being sub-divided into classes each of which contains exactly r immediate reversals. The term in q_l corresponds to a walk with no immediate reversals. The term in q_{l-2} corresponds to a walk with exactly one immediate reversal; this may be specified by the first step of the reversal which can occur at any one of the l steps of the walk (the occurrence at the l th step is interpreted as an improper closure); also there are σ possible directions for this reversal, and when the reversal has been removed we must be left with a non-reversal walk of $(l-2)$ steps. The term in q_{l-4} corresponds to a walk with exactly two immediate reversals which can occur at any pair of the l steps of the walk, and gives rise to the factor ${}^lC_2\sigma^2$ (typical contributions of various terms are illustrated diagrammatically in fig. 12). Similarly the term in q_{l-2r} corresponds to exactly r immediate reversals which give rise to the factor ${}^lC_r\sigma^r$. The final term $B_l(\sigma)$ arises only if l is even and corresponds to walks with no closed configurations, which we may describe as walks on a *Bethe* lattice (§ 4.6);

it can be calculated by putting q_2, q_4, \dots successively equal to zero in (2) and deriving the corresponding r_2, r_4, \dots

If we now apply (2) to (47) we can readily determine the values of q_l as polynomials in σ :

$$\left. \begin{aligned} q_1 &= 0, \\ q_2 &= 0, \\ q_3 &= \sigma(\sigma + 1), \\ q_4 &= \sigma(\sigma + 1)(\sigma - 1), \\ q_5 &= \sigma(\sigma + 1)(\sigma^2 - 3\sigma + 2), \\ q_6 &= \sigma(\sigma + 1)(\sigma^3 - 3\sigma^2 + 5\sigma - 2), \\ q_7 &= \sigma(\sigma + 1)(\sigma^4 - 3\sigma^3 + 7\sigma^2 - 8\sigma + 3). \end{aligned} \right\} \dots \dots \dots (49)$$

Consider now a configuration with v vertices on a close-packed cluster. The v vertices can be chosen in ${}^N C_v$ ways; if we use the symbol p_{lx}^v to denote the corresponding configurational constant (defined per site as before) we may write

$$p_{lx}^v = a_{lx}^v (\sigma + 1) \sigma (\sigma - 1) \dots (\sigma - v + 3), \quad \dots \dots \dots (50)$$

Fig. 12



Analysis of random walk returns. Typical contributions to r_8 . (a) One immediate reversal; (b) Two immediate reversals; (c) Involving no closed configurations.

where the a_{lx}^v are pure numbers independent of σ which can easily be determined by the symmetry of the configuration. Thus $a_6^6 = 1/12$ since a polygon can be described in either direction from any of its vertices; similarly $a_{6c}^5 = 1/8$, $a_{5a}^4 = 1/4$, $a_3^3 = 1/6$. Hence we can calculate configurational constants for close-packed clusters of various sizes, and use them to test topological formulae derived previously.

In particular, if we substitute into (5) from (49) and (50) for close-packed clusters with general σ , and compare the polynomials in σ , we can derive relations which must be satisfied by the path factors $\lambda_{sx}(l)$. It is convenient for this purpose to write (49) in the form

$$q_l = \alpha_l (\sigma + 1) \sigma + \beta_l (\sigma + 1) \sigma (\sigma - 1) + \gamma_l (\sigma + 1) \sigma (\sigma - 1) (\sigma - 2) + \dots \dots \dots (51)$$

where the constants $\alpha_l, \beta_l, \gamma_l \dots$ are easily evaluated numerically. Taking account of the vertex classification we may re-write (5) in the form

$$q_l = \sum_{x; s \leq l} \sum_{v=3}^s \lambda_{sx}{}^v(l) p_{sx}{}^v; \quad . \quad . \quad . \quad . \quad . \quad (52)$$

using (50) and (51) and comparing both sides, we find that

$$\left. \begin{aligned} \sum_{x; s \leq l} \lambda_{sx}{}^3(l) a_{sx}{}^3 &= \alpha_l, \\ \sum_{x; s \leq l} \lambda_{sx}{}^4(l) a_{sx}{}^4 &= \beta_l, \\ \sum_{x; s \leq l} \lambda_{sx}{}^5(l) a_{sx}{}^5 &= \gamma_l, \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (53)$$

the sums being taken over all configurations with 3, 4, 5... vertices respectively. We thus obtain $(l-2)$ relations to be satisfied by the path factors of q_l . For $l=6$ these relations suffice to determine the path factors uniquely; for $l>6$ there are not sufficient relations to determine the path factors but we obtain $(l-2)$ checks on the correctness of the values determined by the direct method.

For checking topological formulae on loose-packed lattices it is convenient to introduce a *loose-packed* cluster of N points (N even) which consists of two equivalent sub-clusters of $N/2$ points, no points in the same sub-cluster being connected, but each point of a sub-cluster being connected to all points of the other sub-cluster (examples are given in fig. 11*b*). It can readily be shown that for a loose-packed cluster $LP(N)$,

$$q_{2l} = \sigma^2 [\sigma^{l-1} + (-1)^l]^2 / (\sigma + 1), \quad . \quad . \quad . \quad . \quad . \quad (54)$$

and we can proceed in a manner closely similar to that for close-packed clusters.

Any homogeneous set of points can be used similarly. For the vertices and edges of the cube, which form a regular set, it is easy to derive the formula

$$r_l = 3(1 + 3^{l-1})/4 \quad (l \text{ even}) \quad . \quad . \quad . \quad . \quad . \quad (55)$$

and hence q_l can be found from (2). The triangular prism (fig. 11*c*) is an example of a homogeneous non-regular set.

It is interesting to observe that the determination of path factors is related to certain classical topological problems. Thus Eulerian paths which arose out of the problem of the Königsberg bridges, are paths on a graph which describe each line of the graph once only (Berge 1958, p. 106). The problem which we have considered is more complicated since we wish to know the number of independent closed paths of l steps, each line of the graph being described at least once. Similarly the problem of Hamiltonian paths and circuits, the specific requirement of which is that no point may be visited more than once (Berge 1958, p. 162), is related to the determination of p_l and c_l for the appropriate configurations. Sykes has used formula (35), and the specific two-dimensional methods to be described in

To derive the partition function per spin we know from §§3.6.1, 3.6.2 that we must put $N=1$ in (56) and (57); for the logarithm of the partition function we must take the coefficient of N . It will be noted that the coefficients of the latter series are all linear in configurational constants, and no configurations with cutting points enter; this result exactly parallels the Mayer theory.

The disappearance of product terms on taking the logarithm is an algebraic property, and does not depend on N being large; it will therefore also be valid for finite clusters of spins†. We can write quite generally

$$\ln Z_N^I = N \ln 2 + \mathcal{N} \ln (\cosh K) + N \sum_{l=1}^{\infty} a_l w^l \quad (w = \tanh K) \quad (58)$$

where the a_l are the linear combinations of lattice constants given by the coefficients of N in (56) and (57). For a finite cluster the series for Z_N^I must terminate after a finite number of terms, and this means that the corresponding combination of constants must be zero for the cluster. In fact we can use the partition functions of finite clusters to obtain some information about the series $\sum a_l w^l$. Because of the linearity of a_l in the lattice constants this series can be put in the alternative form.

$$\sum_{sx} p_{sx} f_{sx}(w) \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

where $f_{sx}(w)$ is a power series in w . Substituting the partition function for a triangle the only lattice constant which enters is p_3 ; hence

$$f_3(w) = \ln(1 + w^3). \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

Similarly for the cluster corresponding to p_{5a} , the only terms which enter are p_3 , p_4 and p_{5a} ; hence we deduce that

$$\left. \begin{aligned} \ln(1 + 2w^3 + w^4) &= 2f_3(w) + f_4(w) + f_{5a}(w), \\ f_{5a}(w) &= \ln \frac{(1 + 2w^3 + w^4)}{(1 + w^3)^2(1 + w^4)} \end{aligned} \right\} \quad . \quad . \quad . \quad (61)$$

This method of deriving the functions $f_{sx}(w)$ is reminiscent of that used by Yvon (1945), Rushbrooke and Scoins (1955), and referred to in §§4.5.1, 4.5.2. The present approach can also deal with non-homogeneous configurations. It can be used to provide high-order approximations in closed form to the no-field partition function; and with its help separated configurations and configurations with cutting points need not be considered for the no-field series.

The series for the magnetic susceptibility in zero field is obtained from eqn. (155) §3.6.2, using the relation

$$\chi_0 = -\partial^2 F / \partial H^2 = kT \frac{\partial^2}{\partial H^2} (\ln Z^I) \quad . \quad . \quad . \quad . \quad (62)$$

(F = Free energy) (H = Magnetic field)

Remembering that

$$\tau = (1 - \mu)/(1 + \mu) = [1 - \exp(-2mH/kT)]/[1 + \exp(-2mH/kT)]$$

we must pick out the terms in τ^2 in the above expansion, and these arise

† This result can best be established rigorously by the use of pseudo-lattices as in §4.5.1.

from configurations with two odd vertices. Some examples of these configurations, which we shall refer to as *magnetic configurations*, are given in fig. 13. It is then easy to derive the formula

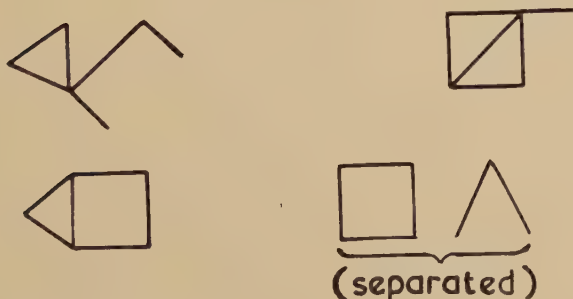
$$\chi_0 = \frac{m^2}{kT} \left[1 + 2 \sum_{l=1}^{\infty} b_l w^l \right] \quad . \quad . \quad . \quad . \quad . \quad (63)$$

where b_l is the coefficient of N in the sum of magnetic configuration constants containing l lines.

For the susceptibility coefficients b_l Sykes derived a theorem analogous to (35) for chains which enables them to be expressed in terms of closed configurations. The relation is

$$b_{l+1} - 2\sigma b_l + \sigma^2 b_{l-1} = \text{Sum of constants of closed configurations of order } (l+1) \text{ or less.} \quad . \quad . \quad . \quad (64)$$

Fig. 13



Some examples of magnetic configurations with six lines.

The configurations which contribute to b_l are considerably more complex than the chains c_l ; hence the proof of this theorem is also somewhat complicated and is given elsewhere (Sykes 1960).

With the aid of (64) we can write (63) in the form

$$\chi_0 = \frac{m^2}{kT} (1 - \sigma w)^{-2} \left[1 - (\sigma - 1)w - \sigma w^2 + \sum_{l=3}^{\infty} d_l w^l \right] \quad . \quad . \quad (65)$$

where the d_l have the following values:

$$\left. \begin{aligned} d_3 &= -6p_3, \\ d_4 &= -8p_4, \\ d_5 &= 6p_3 - 10p_5 + 8p_{5a}, \\ d_6 &= 6p_3 + 8p_4 + 28p_{5a} - 12p_6 + 8(p_{6a} + p_{6b} + p_{6c}), \\ d_7 &= 10p_5 + 36p_{5a} + 16p_{6a} + 30p_{6b} + 16p_{6c} - 14p_7 \\ &\quad + 8(p_{7a} + p_{7b} + p_{7c} + p_{7d} + p_{7e} + p_{7f}) + 44p_{7g}, \\ d_8 &= -6p_3 + 8p_4 - 28p_{5a} + 12p_6 + 56p_{6a} + 24p_{6b} + 8p_{6c} - 48p_{6d} \\ &\quad + 32(p_{7a} + p_{7b} + p_{7c}) + 16(p_{7d} + p_{7e} + p_{7f}) + 8p_{7g} - 16p_8 \\ &\quad + 8(p_{8a} + p_{8b} + p_{8c} + p_{8d} + p_{8e} + p_{8f} + p_{8g} + p_{8h} + p_{8j} + p_{8k} \\ &\quad + p_{8l} + p_{8p} + 6p_{8r} + 6p_{8s}) \end{aligned} \right\} . \quad (66)$$

For loose-packed lattices we can add another term :

$$d_9 = 8p_{7a} + 16(p_{8c} + p_{8h} + 2p_{8r}) + 8(p_{9j} + p_{9k} + p_{9l} + p_{9m}). \quad (67)$$

It will again be noted that the coefficients d_l are linear combinations of the lattice constants p_{sx} . The formulae can be applied as before to finite homogeneous clusters, which can be used to determine the coefficients of particular configuration constants in d_l ; the application to non-homogeneous clusters needs more careful consideration.

No general rule has been given for determining the weight factors of lattice constants in (64) or (66) analogous to those for chains in (35), and in fact these factors must be determined specifically for each configuration. However, Sykes subsequently showed that a further transformation was possible in which the number of constants occurring on the right-hand side of (66) was substantially reduced, and a clear definition of weight factors was possible. If $E(w)$ represents the internal energy, then the series $\sum_3^{\infty} d_l w^l$ in (65) may be put in the form

$$\sum_3^{\infty} d_l w^l = + \frac{2wE(w)}{J} + 8(1+w)^2 \sum_{l=5}^{\infty} g_l w^l, \quad . \quad . \quad . \quad (68)$$

where the g_l are linear sums of lattice constants of order l only which are zero for $l < 5$. The detailed proof of (68) and specification of g_l will be given in the paper by Sykes (1960) referred to above.

Formula (68) has enabled the susceptibility series to be substantially extended, particularly for two-dimensional lattices for which $E(w)$ is known exactly, and 15 terms have been evaluated for the quadratic lattice, 12 for the triangular lattice, and 24 for the honeycomb lattice. Several useful physical conclusions on the form of χ_0 near the Curie point have resulted from the use of (65) and (68). In the case of an antiferromagnetic (for which w must be replaced by $-w$), it has focused attention on the analogy in critical behaviour between $\chi_0(w)$ and $E(w)$ (Fisher and Sykes 1958).

5.3. Mean Values of Configurations

The partition function for the Ising model with general s can be written

$$Z_N^I = \sum_{s_{zi} = -s}^s \prod_{i,j} \exp(4K s_{zi} s_{zj}) \prod_i \exp(2L s_{zi}) \quad (L = mH/2skT). \quad (69)$$

Here we have taken $K = J/4s^2kT$ in accordance with §2.2, so that the maximum and minimum interaction energies remain $\pm J$; the maximum magnetic moment remains m , and we have maintained agreement with our previous results for $s = \frac{1}{2}$.

For the Ising model with $s = \frac{1}{2}$ the relation §3.4.1 (32) means that each bond occurs only once in an expansion of the partition function such as §3.4.1 (33). For $s = 1$ a somewhat analogous treatment is possible, but for general s the exponential must be expanded as follows:

$$\exp(4K s_{zi} s_{zj}) = 1 + 4K(s_{zi} s_{zj}) + \frac{(4K)^2}{2!} (s_{zi} s_{zj})^2 + \dots + \frac{(4K)^r}{r!} (s_{zi} s_{zj})^r. \quad (70)$$

When we substitute the expansion (70) into (69), the term in $(4K)^l$ will still consist of contributions from lines, but multiple occurrences of bonds must be allowed. (Typical configurations are shown in fig. 14.) Also each configuration will be multiplied by an appropriate product of s_{zi} and s_{zj} there being one $s_{zi}s_{zj}$ for each bond; this product must be summed over values of s_{zi} equal to $-s, -(s-1) \dots (s-1), s$. We thus see that each term in the coefficient of $(4K)^l$ consists of two factors, one representing the number of occurrences of a configuration on the lattice, which we denote by C_l and the other which we may call the mean value for the configuration, and which we denote by $\{C_l\}$ (this will be defined precisely later for particular models). If for the configuration C_l the multiplicities of the bonds are $\alpha, \beta, \gamma \dots$ the coefficient of $(4K)^l$ in (70) is

$$\sum C_l \{C_l\} / \alpha! \beta! \gamma! \dots, \quad . \quad . \quad . \quad . \quad . \quad . \quad (71)$$

Fig. 14



Typical configurations with multiple bonds.

the sum being taken over all configurations of l lines.

We may use the tables of lattice constants in Appendix III to determine C_l but we must include a factor to take account of possible change of symmetry; this factor is easily found by inspection, and has the values 3, 4, 6 for the configurations shown in fig. 14 (the appropriate values of

C_l being thus $3p_3, 4p_{5a}, 6 \left[\begin{array}{c} \diagup \quad \diagdown \\ \text{---} \end{array} \right] \left. \vphantom{\begin{array}{c} \diagup \quad \diagdown \\ \text{---} \end{array}} \right)$.

For the Heisenberg model $s_{zi}s_{zj}$ must be replaced by

$$\mathbf{s}_i \mathbf{s}_j (= s_{xi}s_{xj} + s_{yi}s_{yj} + s_{zi}s_{zj})$$

where \mathbf{s} denotes the vector spin operator. The components of \mathbf{s}_i do not commute with one another, and the form (69) is no longer correct and must be rewritten

$$Z_N^{\mathcal{H}} = \left\langle \exp \left[4K \sum_{i,j} \mathbf{s}_i \mathbf{s}_j + 2L \sum_i s_{zi} \right] \right\rangle, \quad . \quad . \quad . \quad . \quad (72)$$

where the brackets $\langle \rangle$ denote the trace. The second term represents the z component of total spin and commutes with the first term. Hence (72) may be rewritten

$$Z_N^{\mathcal{H}} = \left\langle \exp \left(4K \sum_{i,j} \mathbf{s}_i \mathbf{s}_j \right) \prod_i \exp (2L s_{zi}) \right\rangle, \quad . \quad . \quad . \quad . \quad (73)$$

since the various s_{zi} commute among themselves. The exponential can be expanded in powers of $4K$, as before, and contributions of various configurations sorted out. Formula (71) remains valid but now in

calculating the mean value $\{C_l\}$ care must be taken to consider separately all possible permutations of the factors $s_i s_j$ which make up the configuration. The contributions from these permutations will differ because of the non-commutation of the factors, and it is this feature which substantially increases the difficulty of calculations for the Heisenberg model.

5.3.1. Ising model general spin s

Let us define

$$\left. \begin{aligned} t_0 &= \sum_{s_{ji}=-s}^s \exp(2Ls_{ji}) = \mu^{-s} + \mu^{-(s-1)} + \dots + \mu^{(s-1)} + \mu^s. \\ \mu &= \exp(-2L) = \exp(-mH/skT). \end{aligned} \right\} \quad (74)$$

Then in any configuration each free vertex gives rise to a factor t_0 , and the first term in the expansion of (69), corresponding to a configuration with no lines, is t_0^N . Similarly a vertex which is the meeting point of a lines gives rise to a factor

$$t_a = s^a \mu^{-s} + (s-1)^a \mu^{-(s-1)} + \dots + (-s+1)^a \mu^{(s-1)} + (-s)^a \mu^s. \quad (75)$$

We shall take out the factor t_0^N and write $\tau_a = t_a/t_0$. The mean value for a configuration with vertices of multiplicity a, b, c, \dots is then defined by

$$\{C_l\} = \tau_a \tau_b \tau_c \dots \quad (76)$$

and

$$Z_N^I = t_0^N \left[1 + \sum_{l=1}^{\infty} (4K)^l \sum_{\substack{\text{configurations} \\ \text{with } l \text{ lines}}} C_l \tau_a \tau_b \tau_c \dots / \alpha! \beta! \gamma! \dots \right]. \quad (77)$$

In the absence of a magnetic field τ_a are zero for odd a , and only configurations all of whose vertices are even contribute. For the susceptibility in zero field configurations with not more than two odd vertices contribute. To evaluate this susceptibility we must expand each τ_a as far as the second term in H , and pick out the coefficient of H^2 in (77). The coefficients in these expansions are given by successive derivatives of t_0 $[=(\mu^{-s} - \mu^{(s+1)})/(1-\mu)]$ at $\mu=1$, and can readily be obtained from the Taylor expansion of t_0 about $\mu=1$. We find that

$$\left. \begin{aligned} \tau_1 &= -\frac{2X}{3}L + \dots, \\ \tau_2 &= \frac{X}{3} \left[1 + \frac{8X-6}{15}L^2 + \dots \right], \\ \tau_3 &= -\frac{2X}{3} \left[\frac{3X-1}{5}L + \dots \right], \\ \tau_4 &= \frac{X}{3} \left[\frac{3X-1}{5} + \frac{48X^2-76X+30}{105}L^2 + \dots \right], \\ \tau_5 &= -\frac{2X}{3} \left[\frac{3X^2-3X+1}{7}L + \dots \right], \\ \tau_6 &= \frac{X}{3} \left[\frac{3X^2-3X+1}{7} + \frac{40X^3-110X^2+116X-42}{105}L^2 \right], \\ \tau_7 &= -\frac{2X}{3} \left[\frac{35X^3-70X^2+63X-21}{105}L + \dots \right]. \end{aligned} \right\} \quad X=s(s+1), \quad L=mH/2skT, \quad (78)$$

Using (78) and the configurational data of Appendix III series expansions for the partition function and susceptibility in zero field can be written down fairly readily. The expressions are somewhat complicated for general s , and are therefore not reproduced here. Some results for the face-centred cubic lattice are given in the paper by Domb and Sykes (1957b), where the physical conclusions resulting from change of s are also discussed.

5.3.2. Heisenberg model spin $s = \frac{1}{2}$

The major additional difficulty associated with the Heisenberg model is the determination of mean values of non-commutating spin operators for the various configurations. Although in principle the basic problem is the same for all s , we shall consider first the case $s = \frac{1}{2}$, since simplifying features then exist. The mean values for the first four terms in the expansion were first derived by Opechowski (1937), and a serious error was corrected by Zehler (1950). Subsequent additional calculations were performed independently by Rushbrooke and Wood (1955) and Domb and Sykes (1956).

By analogy with (76) we define the mean value $\{C_l\}$ of a configuration by the relation

$$t_0^v \{C_l\} = \left. \left\{ \sum_{\text{permutations}}^{(\text{Av})} \langle (\sigma_i \sigma_j)^\alpha (\sigma_j \sigma_k)^\beta (\sigma_k \sigma_l)^\gamma \dots \prod_i \exp(m H \sigma_{zi} / kT) \rangle \right\} \right\} \quad (79)$$

$$t_0 = (\mu^{-1/2} + \mu^{1/2}).$$

Here the σ_i are the Pauli spin matrices, and the sum is taken over the l lines and v vertices of the configuration;

$$\sum_{\text{permutations}}^{(\text{Av})}$$

denotes the *average* over all the possible different orders of the factors $(\sigma_i \sigma_j)$, $(\sigma_j \sigma_k)$, ... Equation (77) then remains valid with $\tau_a \tau_b \tau_c \dots$ replaced by $\{C_l\}$ as given by (79).

The direct approach to the evaluation of (79) consists in enumerating all permutations for a given configuration, and reducing each permutation using the commutation relations for the σ_j . It is convenient to use suffix notation r, s, t for the coordinates x, y, z and to employ the summation convention; we may thus write

$$\sigma_{rj} \sigma_{sj} = \delta_{rs} + i \epsilon_{rst} \sigma_{tj}. \quad \dots \quad (80)$$

Each product can then be reduced to terms which are linear in σ_{jr} (for each j). For example, for the configuration \triangle_{23}^1 we must reduce

$$(\delta_{rt} + i \epsilon_{rtu} \sigma_{u1}) (\delta_{rs} + i \epsilon_{rst} \sigma_{t2}) (\delta_{st} + i \epsilon_{stw} \sigma_{w3}) = 3 - 2\sigma_{v1} \sigma_{v2} - 2\sigma_{v1} \sigma_{v3} + 2\sigma_{v2} \sigma_{v3} \dots \quad (81)$$

For this product we do not need to consider permutations since the trace of a product of operators is unchanged by cyclic permutations, and points

2 and 3 can be interchanged by symmetry; in the more general case the number of permutations is appreciably reduced by these properties. We must now multiply (81) by $\exp [mH(\sigma_{z1} + \sigma_{z2} + \sigma_{z3})/kT]$ and take the trace of the resulting product. It is easy to see that only σ_z terms will give any contribution; for any particular vertex the absence of a σ_z gives a factor $(\mu^{-1/2} + \mu^{1/2})$ and the presence of a σ_z gives a factor $(\mu^{-1/2} - \mu^{1/2})$. Hence for this configuration

$$\{C\} = 3 - 2\tau^2 \quad [\tau = (1 - \mu)/(1 + \mu)]. \quad \dots \quad (82)$$

Rushbrooke and Wood (1955) showed that a number of elementary relationships could be used to reduce configurations before applying (80). Thus if we denote $\sigma_1\sigma_2$ by (12), we have

$$\left. \begin{aligned} (12)^2 &= 3 - 2(12), \\ (23)[(12) + (13)] &= (12) + (13), \\ (12)(23) + (23)(12) &= 2(13). \end{aligned} \right\} \quad \dots \quad (83)$$

Nevertheless the labour involved in deriving higher terms is large and it is desirable to devise independent means of checking the mean values.

Domb and Sykes (1956) suggested an alternative approach which could be used to derive mean values, and could serve as a check. This alternative method calculates the averages of permutation operators P_{ij} , rather than spin operator $\sigma_i\sigma_j$, using the Dirac relation

$$P_{ij} = \frac{1}{2}(1 + \sigma_i\sigma_j). \quad \dots \quad (84)$$

It is much easier to determine the resultant permutation which is the product of a number of permutation operators; if this resultant permutation is expressed in the form of cycles, each of these cycles can be treated independently, and the averages readily determined. Thus for the

configuration \triangle_{23}^1 considered above,

$$P_{12}P_{23}P_{31} = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} = (1)(23). \quad \dots \quad (85)$$

Taking $\sigma_{z1}, \sigma_{z2}, \sigma_{z3}$ as diagonal, the only diagonal terms in a cyclic permutation correspond to states which remain unchanged by the operation of the permutation, i.e. those for which all elements of the cycle are the same, + or -. Hence the only diagonal terms in (85) are represented by $(+, + +)(+, - -)(-, + +)(-, - -)$ and

$$\langle P_{12}P_{23}P_{31} \exp [H(\sigma_{z1} + \sigma_{z2} + \sigma_{z3})/kT] \rangle = \mu^{-3/2} + \mu^{-1/2} + \mu^{1/2} + \mu^{3/2} \quad \dots \quad (86)$$

To determine the mean value of the P_{ij} interaction as defined by (79) we must divide (86) by $(\mu^{-1/2} + \mu^{1/2})^3$, and we obtain the value

$$(1 + \tau^2)/2. \quad \dots \quad (87)$$

The resulting mean values are tabulated by Sykes (1956) for all configurations of up to six lines, and enable six terms of the complete partition function in a magnetic field to be written down. The zero field partition function and zero field susceptibility agree with the values derived independently by Rushbrooke and Wood and can be written as follows†:

$$\left. \begin{aligned} \ln Z_N^{\mathcal{H}} &= N \ln 2 + \sum_{l=2}^{\infty} e_l K^l / 2^l l!, \\ e_2 &= 3(\sigma + 1)/2, \\ e_3 &= -3(\sigma + 1) + 18p_3, \\ e_4 &= -3(\sigma + 1)(4\sigma + 1) + 72p_4 - 72p_3, \\ e_5 &= 60(\sigma + 1)(2\sigma + 1) - 360p_3(2\sigma + 1) - 480p_4 + 360p_5, \\ e_6 &= 12(\sigma + 1)(44\sigma^2 - 10\sigma + 13) + 216p_3(44\sigma + 3) - 288p_4(20\sigma + 3) \\ &\quad - 3600p_5 - 5904p_{5a} + 2160p_6 - 2880p_{6c} + 288p_{6d}, \end{aligned} \right\} \quad (88)$$

$$\left. \begin{aligned} \frac{kT\chi_0}{m^2} &= 1 + \sum_{l=1}^{\infty} j_l K^l / 2^l l!, \\ j_1 &= (\sigma + 1), \\ j_2 &= 2(\sigma + 1)(\sigma - 1), \\ j_3 &= (\sigma + 1)(6\sigma^2 - 12\sigma - 2) - 60p_3, \\ j_4 &= (\sigma + 1)(24\sigma^3 - 72\sigma^2 + 48\sigma + 40) - 240p_3(2\sigma - 1) - 320p_4, \\ j_5 &= (\sigma + 1)(120\sigma^4 - 480\sigma^3 + 640\sigma^2 + 160\sigma - 104) \\ &\quad - 12p_3(300\sigma^2 - 640\sigma - 140) \\ &\quad - 16p_4(200\sigma - 160) - 2000p_5 + 1440p_{5a}, \\ j_6 &= (\sigma + 1)(720\sigma^5 - 3600\sigma^4 + 6960\sigma^3 - 4064\sigma^2 - 5168\sigma - 1232) \\ &\quad - 12p_3(2400\sigma^3 - 8280\sigma^2 + 3504\sigma - 816) - 16p_4(1800\sigma^2 \\ &\quad - 4992\sigma) - 20p_5(1200\sigma - 1128) + 8p_{5a}(2160\sigma + 3888) \\ &\quad - 14400p_6 + 9792p_{6a} \\ &\quad + 9216p_{6b} + 29568p_{6c} + 3072p_{6d}. \end{aligned} \right\} \quad (89)$$

As an additional check on the mean values Domb and Sykes evaluated the exact partition functions for finite clusters such as



and expanded them in the same manner as (77) (using the mean values defined by (79)); if different interactions are used for different bonds

(e.g. )

the mean values for configurations with repeated lines can be derived

† The subsequent calculations of Rushbrooke and Wood 1958 for general s enable the term e_7 to be added.

directly. For homogeneous clusters direct verification by substitution is possible in formulae such as (88) and (89).

The physical conclusions to be drawn from the application of formulae (88) and (89) have been discussed in the papers by Domb and Sykes and Rushbrooke and Wood. For the Heisenberg model it seems clear that additional terms in these formulae could be very useful; however, the methods described above do not seem capable of extension without very great labour. Domb and Sykes (to be published) have therefore recently investigated an approach rather like that of (59) in which the free energy is expressed as a sum of contributions from finite clusters. Repeated factors and permutations would then be avoided, but open configuration cannot be eliminated for the Heisenberg model, and must be taken into account.

We shall illustrate the method by writing down the first three terms of the expansion. The finite configurations required are



the lattice constants of which we denote by $p_1^{(1)}, p_2^{(1)}, p_3^{(1)}, p_3^{(2)}, p_3$; we denote the corresponding free energies by $f_1^{(1)}, f_2^{(1)}, f_3^{(1)}, f_3^{(2)}, f_3$. The free energy for a general lattice can then be written in the form

$$F = N[p_1^{(1)}\phi_1^{(1)} + p_2^{(1)}\phi_2^{(1)} + p_3^{(1)}\phi_3^{(1)} + p_3^{(2)}\phi_3^{(2)} + p_3\phi_3 + \dots]. \quad (90)$$

But this formula applies equally to any cluster. Hence applying it successively to the above configurations we deduce that

$$\left. \begin{aligned} f_1^{(1)} &= \phi_1^{(1)}, \\ f_2^{(1)} &= 2\phi_1^{(1)} + \phi_2^{(1)}, \\ f_3^{(1)} &= 3\phi_1^{(1)} + 3\phi_2^{(1)} + \phi_3^{(1)}, \\ f_3^{(2)} &= 3\phi_1^{(1)} + 2\phi_2^{(1)} + \phi_3^{(2)}, \\ f_3 &= 3\phi_1^{(1)} + 3\phi_2^{(1)} + \phi_3, \end{aligned} \right\} \dots \dots \dots (91)$$

from which the ϕ 's can readily be obtained in terms of the f 's. High-temperature expansions for finite clusters can be obtained from the traces of powers of matrices, and it is possible that computers could hence be put to effective use for this problem.

5.3.3. Heisenberg model general spin s

The extension of high-temperature series expansions for the Heisenberg model to general s was carried out by Brown and Luttinger (1955) who derived four terms of the susceptibility expansion. A comprehensive attack on the problem was subsequently provided by Rushbrooke and Wood (1957, 1958) who obtained two additional terms of this expansion (incidentally correcting a small error in a calculation of the fifth term by Brown (1956)).

The mean values for any configuration for general s depend on the multiplicities of the vertices, as for the Ising model (§ 5.3.1.), and will be functions of the τ 's; but the traces of products of spin operators must be averaged over all possible permutations as in the previous section. The properties of spin operators for general s can be handled in the standard manner by taking s_z as diagonal and introducing $s^+ = s_x + is_y$, $s^- = s_x - is_y$ (Mandl 1954). In terms of these operators, the Heisenberg interaction can be written

$$\mathbf{s}_i \mathbf{s}_j = s_{zi} s_{zj} + \frac{1}{2}(s_i^+ s_j^- + s_i^- s_j^+). \quad (92)$$

Operators corresponding to different vertices commute, and in any product of operators corresponding to a single vertex, the only diagonal terms are those with equal numbers of s^+ and s^- operators. Also

$$\begin{aligned} s^+ s^- &= s(s+1) + \hbar s_z - s_z^2, & s^+ s_z - s_z s^+ &= -\hbar s^+, \\ s^- s^+ &= s(s+1) - \hbar s_z - s_z^2, & s^- s_z - s_z s^- &= \hbar s^-, \end{aligned}$$

and with the aid of these relations the diagonal terms in a product of operators can be reduced as polynomials in s_z . When we multiply by $\exp(2Ls_{zi})$ and take the trace by summing over the $(2s+1)$ possible values of s_{zi} , each s_{zi}^a gives rise to a term τ_a , as for the Ising model. In this manner we could obtain the complete partition function in the presence of a magnetic field. However, we are mostly interested in expansions for the partition function and susceptibility in zero field, and Rushbrooke and Wood (1958) showed that if the terms in these expansions were considered directly, a considerable simplification arose because of the symmetry of the spin operators in x, y, z .

For the no-field series by analogy with (79) the required mean values are given by

$$(2s+1)^v \{C_{U^0}\} = \sum_{\text{permutations}}^{(Av)} \langle (\mathbf{s}_i \mathbf{s}_j)^\alpha (\mathbf{s}_j \mathbf{s}_k)^\beta (\mathbf{s}_k \mathbf{s}_l)^\gamma \dots \rangle. \quad (93)$$

Rushbrooke and Wood (1958) give an example of a particular calculation for the configuration



There are twelve permutations of the product (93):

$$\begin{array}{llll} (12) (12) (13) (23) & (12) (13) (23) (12) & (13) (12) (23) (12) \\ (12) (12) (23) (13) & (12) (23) (13) (12) & (23) (12) (13) (12) \\ (12) (13) (12) (23) & (13) (12) (12) (23) & (13) (23) (12) (12) \\ (12) (23) (12) (13) & (23) (12) (12) (13) & (23) (13) (12) (12) \end{array}$$

Because of the invariance of the trace under cyclic permutations only three of these products need be considered, $(12) (12) (13) (23)$, $(12) (12) (23) (13)$ and $(12) (13) (12) (23)$, and of these the first two must be equal by symmetry

in 1 and 2. Using suffixes $r, s, t, u \dots$ for x, y, z as before, and summation convention, the right-hand side of (93) may be written

$$\begin{aligned} & \frac{1}{3} [2s_{1r}s_{2r}s_{1t}s_{2t}s_{1u}s_{3u}s_{2v}s_{3v} + s_{1r}s_{2r}s_{1t}s_{3t}s_{1u}s_{2u}s_{2v}s_{3v}] \\ &= \frac{1}{3} [2(s_{1r}s_{1t}s_{1u})(s_{2r}s_{2t}s_{2v})(s_{3u}s_{3r}) + (s_{1r}s_{1u}s_{1t})(s_{2r}s_{2t}s_{2v})(s_{3t}s_{3v})]. \end{aligned} \quad (94)$$

Now it is easy to show that the only products of two spin operators giving non zero trace are

$$\langle s_x^2 \rangle = \langle s_y^2 \rangle = \langle s_z^2 \rangle = \frac{1}{3} \langle s^2 \rangle = \frac{1}{3} (2s+1)X \quad [X = s(s+1)] \quad . \quad . \quad (95)$$

and the only corresponding products of three spin operators are

$$\langle s_x s_y s_z \rangle = -\langle s_x s_z s_y \rangle = \frac{1}{6} i (2s+1)X. \quad . \quad . \quad . \quad (96)$$

Hence we find that (94) reduces to

$$\frac{1}{3} [6 \langle s_x s_y s_z \rangle^2 \langle s_x^2 \rangle],$$

and that for this configuration, from (93)

$$\{C_{ij}\}_0 = -\frac{1}{54} X^3. \quad . \quad . \quad . \quad . \quad . \quad (97)$$

Fig. 15



Number of independent permutations to be considered in various configurations for the Heisenberg model (after Rushbrooke and Wood).

All configurations must be treated in this manner, and for the higher terms the work is very lengthy. Figure 15 represents a number of configurations, and the corresponding number of permutations to be taken into account. Rushbrooke and Wood list all non-zero traces, such as (95) and (96), of products of up to seven spin operators. They also enunciate a theorem which sometimes reduces the work entailed by the loosely bound configurations, such as simple polygons.

Theorem I. If a connected configuration C_i has somewhere three consecutive single lines (ij) (jk) (km) , the points j and k being not otherwise involved in the configuration, and if C_{i-1} is the configuration obtained by

removing the centre one, (jk) , of these lines, and making j and k coincide (the other points of the diagram remaining unchanged) then

$$\{C_{l0}\} = \frac{1}{3}(1 + \delta_{im})lX\{C_{l-1}\}_0. \quad (98)$$

where $\delta_{im} = 1$ if the points i and m coincide and 0 otherwise.

Rushbrooke and Wood (1958) then proceed to show that even for the zero-field susceptibility expansion only traces similar to those in (93) need be evaluated. To see this we must replace σ_i by s_i in (79) and expand $\{C_l\}$ as far as the second order in H . The first order terms in H are zero since there is no spontaneous magnetization; and the second order terms involve averages like

$$\sum_{\text{permutations}}^{(Av)} \langle (s_i s_j)^\alpha (s_j s_k)^\beta (s_k s_l)^\gamma \dots s_{zp} s_{zq} \rangle \quad (99)$$

where p and q are any two points of the lattice. Again all possible permutations must be considered, but only of the s_j in C_l and not of s_{zp}, s_{zq} . The configurations involved in (99) may be represented by a set of l lines and two crosses (corresponding to p and q). The two crosses may lie on the configuration C_l or be partially or wholly separated from it; they may also coincide in which case they will be referred to as a double cross. Rushbrooke and Wood then give three theorems which show that double crosses and separated crosses can be ignored; and that averages for a configuration C_l with two crosses can be replaced by averages for a new configuration C_{l+1} without crosses. We shall use the symbol C_l^+ to represent a configuration with a single cross, C_{l+}^+ a configuration with a double cross, and C_l^{++} a configuration with two single crosses. Mean values are defined in the same way as (93), but v on the left-hand side corresponds to the number of vertices of the new configuration with crosses added. We then have

Theorem II.

$$\{C_{l+}^+\} = \frac{1}{3}X\{C_l\}_0. \quad (100)$$

This follows readily from the relation

$$\begin{aligned} \langle (s_i s_j)^\alpha (s_j s_k)^\beta (s_k s_l)^\gamma \dots s_{zp}^2 \rangle &= \langle (s_i s_j)^\alpha (s_j s_k)^\beta (s_k s_l)^\gamma \dots s_{yp}^2 \rangle \\ &= \langle (s_i s_j)^\alpha (s_j s_k)^\beta (s_k s_l)^\gamma \dots s_{xp}^2 \rangle = \frac{1}{3} \langle (s_i s_j)^\alpha (s_j s_k)^\beta (s_k s_l)^\gamma \dots s_p^2 \rangle, \end{aligned} \quad (101)$$

since s_p^2 is constant and equal to X . When the double cross is separated there is an extra $(2s+1)$ in the trace, but this is cancelled by the extra vertex. As a consequence of this theorem double crosses make no contribution to the susceptibility, since the coefficient of N in the total number of configurations C_{l+}^+ is zero.

Theorem III.

$$\{C_l^+\} = 0. \quad (102)$$

The reduction of such a diagram yields only odd powers of s_z and hence the trace is zero. This is related to the vanishing of the first order terms in the expansion of the free energy with respect to H .

Theorem IV. If C_l^{++} has crosses at points i and j of a configuration and C_{l+1} is the configuration obtained by replacing the crosses by the line ij (whether i and j are neighbouring lattice points or not) then

$$\{C_l^{++}\} = \frac{1}{3}\{C_{l+1}\}_0. \quad . \quad . \quad . \quad . \quad . \quad (103)$$

This follows from the relation

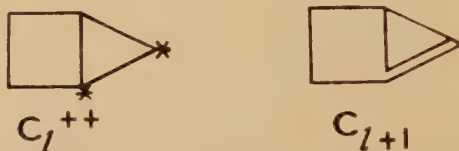
$$\begin{aligned} \langle (\mathbf{s}_i \mathbf{s}_j)^\alpha (\mathbf{s}_j \mathbf{s}_k)^\beta (\mathbf{s}_k \mathbf{s}_l)^\gamma \dots s_{z\rho} s_{zq} \rangle &= \langle (\mathbf{s}_i \mathbf{s}_j)^\alpha (\mathbf{s}_j \mathbf{s}_k)^\beta (\mathbf{s}_k \mathbf{s}_l)^\gamma \dots s_{yp} s_{yq} \rangle \\ &= \langle (\mathbf{s}_i \mathbf{s}_j)^\alpha (\mathbf{s}_j \mathbf{s}_k)^\beta (\mathbf{s}_k \mathbf{s}_l)^\gamma \dots s_{x\rho} s_{xq} \rangle = \frac{1}{3} \langle (\mathbf{s}_i \mathbf{s}_j)^\alpha (\mathbf{s}_j \mathbf{s}_k)^\beta (\mathbf{s}_k \mathbf{s}_l)^\gamma \dots (\mathbf{s}_p \mathbf{s}_q) \rangle. \end{aligned} \quad . \quad . \quad . \quad . \quad (104)$$

The right-hand side is one of the permutations of $\{C_{l+1}\}_0$ and each permutation can be treated similarly since $s_{z\rho} s_{zq}$ can be fitted in equally well at any point in the product. In counting the number of C_l^{++} we must remember a factor 2 arising from the cross-terms in the product

$$\prod_i \exp(2Ls_{zi}).$$

A typical example of C_l^{++} and C_{l+1} is shown in fig. 16.

Fig. 16



A typical example of C_l^{++} and C_{l+1} . Susceptibility configurations (with crosses) can be replaced by normal configurations.

As a consequence of theorems III and IV configurations which fall into two parts on the removal of a single line can be ignored. For on replacing the line by crosses at each end it is clear that the trace of the configuration vanishes.

Rushbrooke and Wood determined the zero field mean values of all configurations required for six terms of the susceptibility series (88) (which are polynomials in X .) As a result they derived six terms of the series (88) and seven terms of the series (89) for general s . The results are somewhat complicated, and we therefore do not reproduce them here.

5.4. Low Temperature Lattice Constants

5.4.1. Closed configurations

We have discussed briefly the nature of low-temperature configurations in §5.1.2, and introduced the notation to be used. We have also seen in §5.2.1. that the classification of configurations into space types enables

low-temperature lattice constants to be determined. In fact for low-temperature expansions tightly bound configurations like P_{6d} play a very significant part, and the method of space types becomes particularly important; the analytic methods employed for high-temperature lattice constants are correspondingly less useful. However, algebraic relations can be derived between high- and low-temperature lattice constants which enable the latter to be calculated.

In a low-temperature configuration none of the vertices unconnected by lines may be nearest neighbours, whereas for high temperature configurations no such restriction exists. For close-packed configurations in which all pairs of vertices are connected the high-temperature and low-temperature lattice constants are the same; thus $p_3 = P_3$, $p_{6d} = P_{6d}$. Close-packed configurations with five vertices (10 lines) do not exist on any of the lattices we have considered. A configuration of five vertices and nine lines exists on the hexagonal close-packed lattice P_{9n} ;



the high-temperature lattice constant would enter only at the tenth term of the susceptibility series. For the face-centred cubic lattice the maximum number of lines for a configuration with five vertices is eight. There are two such configurations P_{8q} and P_{8u} and for both of these we have $p_{8q} = P_{8q}$, $p_{8u} = P_{8u}$; however, the latter was not tabulated among the high-temperature lattice constants since it enters the series (56) and (66) only at a much later stage.

Let us now consider the relation between p_{5a} and P_{5a} . If we examine all the p_{5a} we find that we include all the P_{5a} when the unconnected opposite vertices are not nearest neighbours, and all the P_{6d} when they are nearest neighbours; each P_{6d} will occur six times since there are six independent p_{5a} on a tetrahedron. Hence we have

$$p_{5a} = P_{5a} + 6P_{6d}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (105)$$

Similarly, if we examine all the p_4 we shall include P_4 once, P_{5a} once, and P_{6d} three times. Hence

$$p_4 = P_4 + P_{5a} + 3P_{6d}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (106)$$

In Appendix IV we have tabulated low-temperature lattice constants of closed configurations arising from five spins or less for the lattices considered previously. For larger numbers of spins the lattices are best treated individually. Thus for the simple quadratic lattice constants have been evaluated for configurations of up to 10 spins, and for the simple cubic and body-centred cubic lattices for configurations of up

to eight spins; however, for the face-centred cubic lattice the number of configurations which enter increases rapidly, and is quite large even for six spins.

5.4.2. *Open and separated configurations*

The method of evaluating open configurations is closely similar to that described in §5.2.6, but when we attach a single bond, we must take account of the nearest neighbours of its free end. Thus if we attach a single bond to P_4 we can form



as in §5.2.6, but also P_{6a} , P_{6b} , P_{7h} , P_{8u} . (However, not P_{5a} since opposite vertices of P_4 cannot be nearest neighbours.) Hence instead of (34) we have

$$4(\sigma-1)P_4 = \left[\text{square with bond} \right] + 6P_{6a} + 2P_{6b} + 6P_{7h} + 4P_{8u}. \quad (107)$$

Similarly low-temperature lattice constants for reducible configurations (e.g. P_{5a} , P_{6c}) can be calculated directly by a method analogous to §5.2.4.

For separated configurations we follow the procedure of §5.2.7. Thus by putting together a single spin and a triangle we derive the relation

$$N^2P_3 = N[P_3, \bullet] + N \left[\text{triangle with bond} \right] + 3NP_3 + 2NP_{5a} + 4NP_{6d},$$

and hence it is easy to show that

$$[P_3, \bullet] = N^2P_3 - 3\sigma P_3 + 2P_{5a} + 8P_{6d}. \quad (108)$$

We shall see shortly that by means of certain algebraic transformations all configurations which are not multiply-connected can be eliminated in deriving low-temperature series for the simple Ising model. Nevertheless this procedure introduces complications in the actual derivation of terms of the series, and other configurational problems on crystals involve lattice constants of all configurations. We have therefore reproduced in Appendix IV the lattice constants corresponding to all configurations consisting of up to five overturned spins.

5.4.3. *Low-temperature series expansion for the Ising model*

We have already discussed the form of the low temperature series expansion in §3.6.1 as follows (§3 eqn. (143)):

$$\Lambda(\mu, z) = 1 + \mu f_1(z) + \mu^2 f_2(z) + \dots + \mu^l f_l(z) + \dots$$

We also derived the first few terms for the simple quadratic lattice. These

terms can be written in general form in terms of low-temperature lattice constants as follows:

$$\begin{aligned}
 f_1(z) &= z^q, \\
 f_2(z) &= z^{2q} \left[\frac{q}{2} z^{-2} - \frac{q}{2} \right], \\
 f_3(z) &= z^{3q} \left\{ P_3 z^{-6} + \left[\frac{q(q-1)}{2} - 3P_3 \right] z^{-4} + \left[\frac{-q(2q-1)}{2} \right. \right. \\
 &\quad \left. \left. + 3P_3 \right] z^{-2} + \left(\frac{q^2}{2} - P_3 \right) \right\}, \\
 f_4(z) &= z^{4q} \left\{ P_{6d} z^{-12} + P_{5a} z^{-10} + [P_4 + 3P_3(q-2) - 4P_{5a} - 12P_{6d}] z^{-8} \right. \\
 &\quad + \left[\frac{q(q-1)(4q-5)}{6} - P_3(12q-21) - 4P_4 + 6P_{5a} + 28P_{6d} \right] z^{-6} \\
 &\quad + \left[\frac{q}{8} (-16q^2 + 25q - 10) + 3P_3(6q-7) + 6P_4 - 4P_{5a} - 27P_{6d} \right] z^{-4} \\
 &\quad + \left[\frac{q}{4} (8q^2 - 7q + 2) - 3P_3(4q-3) - 4P_4 + P_{5a} + 12P_{6d} \right] z^{-2} \\
 &\quad \left. + \left[-\frac{q}{24} (16q^2 - 3q + 2) + P_3(3q-1) + P_4 - 2P_{6d} \right] \right\}. \quad (109)
 \end{aligned}$$

Here the final term in the polynomial $f_t(z)$ corresponding to z^{tq} arises from t separated spins, the term before this to t spins with one bond, and so on, the first term corresponding to the most tightly bound configuration with the maximum number of bonds.

It was shown by Domb (1949) that only a portion of the coefficients in the polynomials $f_t(z)$ need be determined, and the remainder can automatically be calculated by algebraic manipulation. We shall illustrate the method by considering the simple quadratic lattice, but the results apply equally to any other of the lattices considered; if we start by determining most tightly bound configurations we will find that only configurations with t spins and t or more bonds need be considered. For the simple quadratic lattice we have

$$\begin{aligned}
 \Lambda &= 1 + \mu u^2 + \mu^2(2u^3 - 2u^4) + \mu^3(6u^4 - 14u^5 + 8u^6) + \mu^4(u^4 + 18u^5 - 77u^6 \\
 &\quad + 98u^7 - 40u^8) + \dots \quad (u = z^2). \quad . \quad . \quad . \quad . \quad . \quad (110)
 \end{aligned}$$

This is best regarded as a low-density expansion in μ valid in the neighbourhood of DE (§3 fig. 38). If we put $u = 1$ in (110) we find that the $\Lambda = 1 + \mu$, and this is the result we should expect in the limit of infinite temperatures (§3, eqn. (156)). Hence $f_t(1) = 0$ for all $t > 1$ and we have one relation between the coefficients of $f_t(z)$.

We can now proceed to find an expansion near $u = 1$. Putting $(1 - u) = \zeta$, and expanding Λ as a power series in ζ , the coefficient of ζ is

$$-2\mu + 2\mu^2 - 2\mu^3 + 2\mu^4 - \dots \quad . \quad . \quad . \quad . \quad . \quad (111)$$

and we may assume that the sum of this is $-2\mu/(1+\mu)$. Similarly the coefficient of ζ^2 is

$$\mu - 6\mu^2 + 16\mu^3 - 31\mu^4 + \dots, \quad (112)$$

and in this series second differences of coefficients are constant; this indicates that the sum is $(\mu - 3\mu^2 + \mu^3)/(1+\mu)^3$. We are thus tempted to postulate a general expansion of the form

$$\Lambda = (1+\mu) + \sum_{r=1}^{\infty} \frac{\psi_r(\mu)\zeta^r}{(1+\mu)^{2r-1}} \quad (113)$$

where the $\psi_r(\mu)$ satisfy the relation

$$\psi_r(\mu^{-1}) = \mu^{-2r}\psi_r(\mu). \quad (114)$$

In fact the expansion (113) is a consequence of §3 eqn. (156), when we remember that $\phi_r(\tau)$ is a polynomial in τ^2 whose maximum power is τ^{2r} .

Thus we see that from (111) and (112) we can deduce the values of the first two derivatives at $z=1$, $f_t^{(1)}(1)$, $f_t^{(2)}(1)$ for all t . In general from a knowledge of $f_1(u) \dots f_{t-1}(u)$ we can deduce $f_t(1)$, $f_t^{(1)}(1)$, \dots , $f_t^{(t-1)}(1)$, and hence t relations between the coefficients of the polynomial $f_t(u)$.

If we consider the expansion of $\ln \Lambda$ we have seen by analogy with the Mayer theory (§4.5.1) that separated configurations can be eliminated, and if we write as in §3, eqn. (146):

$$\ln \Lambda(\mu, z) = \mu g_1(z) + \mu^2 g_2(z) + \dots \mu^t g_t(z) + \dots$$

the $g_i(z)$ will all depend linearly on the lattice constants (although the terms of $f_i(z)$ given in (109) depend linearly on the lattice constants, $f_6(z)$ would bring in P_3^2 from separated triangles and similarly for higher terms). We may write the first four terms as follows:

$$\begin{aligned} g_1(z) &= z^q, \\ g_2(z) &= z^{2q} \left[\frac{q}{2} z^{-2} - \frac{(q+1)}{2} \right], \\ g_3(z) &= z^{3q} \left\{ P_3 z^{-6} + \left[\frac{q(q-1)}{2} - 3P_3 \right] z^{-4} + (3P_3 - q^2) z^{-2} \right. \\ &\quad \left. + \left[\frac{q(q+1)}{2} - P_3 + \frac{1}{3} \right] \right\}, \\ g_4(z) &= z^{4q} \left\{ P_{6d} z^{-12} + P_{5a} z^{-10} + [P_4 + 3P_3(q-2) - 4P_{5a} - 12P_{6d}] z^{-8} \right. \\ &\quad + \left[\frac{q(q-1)(4q-5)}{6} - 3P_3(4q-6) - 4P_4 + 6P_{5a} + 28P_{6d} \right] z^{-6} \\ &\quad + \left[-\frac{q(8q^2-10q+3)}{4} + 18P_3(q-1) + 6P_4 - 4P_{5a} - 27P_{6d} \right] z^{-4} \\ &\quad + \left[\frac{q(4q^2-q+1)}{2} - 6P_3(2q-1) - 4P_4 + P_{5a} + 12P_{6d} \right] z^{-2} \\ &\quad \left. + \left[-\frac{1}{4} - \frac{q(8q^2+6q+7)}{12} + 3qP_3 + P_4 - 2P_{6d} \right] \right\}. \quad (115) \end{aligned}$$

However it will be seen that the general expression is rather complicated.

If we now introduce the variable $f = (z^{-2} - 1)$ as in the Mayer theory (§4.5.1) we might expect an appreciable simplification. We shall express,

the result in terms of high temperature lattice constants since these arise naturally in the Mayer development. We find that

$$\left. \begin{aligned} g_1(z) &= z^q, \\ g_2(z) &= z^{2q} \left[\frac{q}{2} f - \frac{1}{2} \right], \\ g_3(z) &= z^{3q} \left[p_3 f^3 + \frac{q(q-1)}{2} f^2 - qf + \frac{1}{3} \right], \\ g_4(z) &= z^{4q} \left\{ p_{6d} f^6 + p_{5a} f^5 + p_4 f^4 - 3p_3 f^3 + \frac{q(q-1)(q-2)}{6} f^3 \right. \\ &\quad \left. + \left[\frac{q(q-1)^2}{2} - 3p_3 \right] f^3 - 2q(q-1)f^2 - \frac{1}{4} q f^2 + \frac{3}{2} q f - \frac{1}{4} \right\}. \end{aligned} \right\} \quad (116)$$

We have written the contributions in such a manner that they can readily be identified with appropriate configurations. Thus for $g_4(z)$ all connected configurations with four vertices or less enter as follows:

$$p_{6d}, p_{5a}, p_4, p_3, \quad \text{Y}, \quad \text{Z}, \quad \text{V}, \quad / , \quad \bullet \quad \bullet$$

Proceeding with the Mayer theory and expressing $\ln \Lambda$ as a power series in

$$\alpha_1 = \mu \frac{\partial}{\partial \mu} (\ln \Lambda)$$

in the form

$$\ln \Lambda(\alpha_1, z) = \alpha_1 h_1(z) + \alpha_1^2 h_2(z) + \dots \alpha_u h_u(z) + \dots$$

we find that

$$\left. \begin{aligned} h_1(z) &= 1 \\ h_2(z) &= -\frac{g_2}{g_1^2} = \frac{1}{2} - \frac{q}{2} f \\ h_3(z) &= -\frac{2g_3}{g_1^3} + \frac{4g_2^2}{g_1^4} = \frac{1}{3} + qf^2 - 2p_3 f^3 \\ h_4(z) &= -\frac{3g_4}{g_1^4} + \frac{18g_3g_1}{g_1^4} - \frac{20g_2^3}{g_1^6} = \frac{1}{4} + q\left(-\frac{5}{2}f^3 - \frac{3}{4}f^2\right) \\ &\quad + 9p_3(2f^4 + f^3) - 3p_4 f^4 - 3p_{5a} f^5 - 3p_{6d} f^6. \end{aligned} \right\} \quad (117)$$

A comparison between (117) and (109) shows strikingly the great simplification produced by the changes of variable in accordance with the Mayer theory; in (117) only lattice constants of multiply-connected configurations enter. Comparing (117) with §4 (82) we see that

$$h_{u+1}(z) = -\frac{u}{u+1} \beta_u(z). \quad \dots \quad (118)$$

Several of the terms contributing to $h_u(z)$ can be derived from the results of Rushbrooke and Scoins (1955). Thus from §4 (87) it is clear that the term independent of lattice constants is equal to $1/u$. Similarly expanding §4 (90) in powers of α_1 we find that

$$\frac{1}{2} H_2(\alpha_1, z) = -\frac{1}{2} \alpha_1^2 f + \alpha_1^3 f^2 - \alpha_1^4 \left(\frac{3}{4} f^2 + \frac{5}{2} f^3 \right) + \dots \quad (119)$$

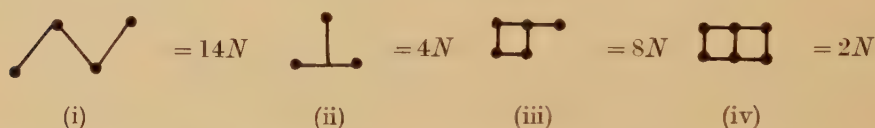
which checks with (117). Terms in p_3 and p_4 can be derived in the same manner from §4 (91). This method cannot be applied to lattice constants.

of non-homogeneous configurations, although it seems likely that the more general formulae of Yvon §4 (105), (107) and (111) could be used. Alternatively, direct calculation can be undertaken from §4 (83) starting with the given configuration having one system at each vertex, and then considering the possibility of multiple occupation of the vertices.

5.4.4. *Special methods for two-dimensional lattices*

All the methods so far described can be used to derive irreducible constants on two-dimensional lattices but it is usually easier to exploit the dual-net property mentioned in §3.4.2.

The method is best illustrated by an example. The simple quadratic lattice is self-dual and every connected low-temperature configuration of t spins and r bonds corresponds to an arrangement of $l = qt - 2r$ bonds with a connected interior on the dual lattice. For small values of l all such arrangements must be polygons, and for $l=10$ the only possible partitions are $t=4, r=3$; $t=5, r=5$; $t=6, r=7$ and from Appendix IV we see that these correspond to the low-temperature configurations in fig. 17*a*. We thus deduce at once that there are $18N$



decagons of area 4, $8N$ decagons of area 5 and $2N$ decagons of area 6 and that $p_{10}=28$. It is not necessary to specify the individual space types and the low-temperature configurations provide a systematic way of enumerating polygons on a plane lattice. For larger values of l not all structures with a connected interior are simple polygons but the exceptional cases are not difficult to allow for (e.g. fig. 17*b*) and the method has been used to derive p_{14} , p_{16} and p_{18} for the simple quadratic lattice. In a similar way polygons on the triangular lattice may be obtained by enumerating the corresponding duals on the honeycomb lattice.

The dual lattice also provides a convenient way of evaluating other high-temperature lattice constants. For example, the number of polygons with a single bridge can be determined by considering the possibility of crossing single bonds in the low-temperature configurations of fig. 17*a*; it is easy to see that there are $42N$ from (i), $12N$ from (ii) $8N$ from (iii) and none from (iv), and these can be sorted into various categories. Similarly polygons with double bridges arise from the possibility of crossing certain pairs of bonds in the low-temperature configurations. These can only occur with polygons of types (iii) and (iv) there being six possible double bridges in each case.

5.4.5. *Low-temperature antiferromagnetic expansions*

As remarked in §3.6.1, low-temperature antiferromagnetic expansions can be derived for lattices which can be decomposed into two equivalent

are aligned against the applied field. The contribution of the second type will be $\frac{1}{2}N(\frac{1}{2}N-4)y^8$. The sorting out of the low temperature configurations given in Appendix IV into sub-lattices is tedious but straightforward and the series given by Brooks and Domb (1951) for the simple quadratic lattice is readily derived. The corresponding series for the simple cubic lattice has been given by Wakefield (1951).

One might again expect a substantial simplification to arise from the application of the Mayer theory, and an approach of this kind has been initiated by Temperley (1959). Alternatively it seems very likely that the method of Yvon (§ 4.5.2.) could be usefully applied to this problem in a manner similar to § 5.4.3.

Notation for § 5

Configurations classified by p points and l lines, $\sigma = q - 1$, q coordination number of lattice.

Typical high-temperature lattice constant of l lines p_{lx} .

Simple closed polygons p_v , simple chains c_l . (If we wish to record the number of vertices v of the configuration we write p_{lx}^v).

Typical low-temperature lattice constant of l lines P_{lx} .

Lattice constants of separated configurations $[p_{lx}, p_{my}]$ $[P_{lx}, P_{my}]$.

r_l number of returns to the origin in a random walk of l steps.

q_l number of returns to the origin in a no-reversal random walks of l steps (excluding improper closures).

$\lambda_{sx}(l)$ path factor of configuration p_{sx} in random walk of l steps.

$\phi(x, y, z)$ generating function for random walks on a lattice.

$\psi(x, y, z)$ generating function for no-reversal random walks on a lattice.

$R_l(a, b, c)$ numbers of walks arriving at (a, b, c) after l steps.

$Q_l(a, b, c)$ number of no-reversal walks arriving at (a, b, c) after l steps.

$w = \tanh K = \frac{1-z}{1+z}$ = variable for high-temperature expansions.

b_l, d_l coefficients in susceptibility expansion for Ising model ($s = \frac{1}{2}$) [eqn. (63), (65)].

C_l number of occurrences of a general configuration (with multiple bonds) on the lattice.

$\{C_l\}$ mean value of this configuration.

$Z_N^{\mathcal{H}}$ partition function for Heisenberg model.

$t_a = s^a \mu^{-s} + (s-1)^a \mu^{-(s-1)} + \dots + (-s+1)^a \mu^{(s-1)} + (-s)^a \mu^s$, $\tau_a = t_a/t_0$.

e_i, j_i coefficients in susceptibility expansion for Heisenberg model ($s = \frac{1}{2}$) [eqns. (88), (89)].

$f_r(z), g_r(z), \phi_r(\tau)$ as in § 3.

$u = z^2, \zeta = 1 - u, \psi_r(\mu)$ defined by (113), $h_r(z)$ by (117), $H_{ix}(\alpha_1, z)$ by § 4 (86).

APPENDIX I

ANALYSIS OF RETURNS TO THE ORIGIN IN A RANDOM WALK

(a) Simple quadratic lattice

$$\begin{aligned}
 r_2 = 4 &= 2 \left[\text{—} \right]_{(2)} \\
 r_4 = 36 &= 2 \left[\text{—} \right]_{(2)} + 4 \left[\text{^} \right]_{(6)} + 8 \left[\square \right]_{(1)} \\
 r_6 = 400 &= 2 \left[\text{—} \right]_{(2)} + 12 \left[\text{^} \right]_{(6)} + 6 \left[\text{^} \right]_{(18)} + 12 \left[\text{>} \right]_{(4)} \\
 &\quad + 48 \left[\square \right]_{(1)} + 12 \left[\square \right]_{(8)} + 12 \left[\text{hexagon} \right]_{(2)} \\
 r_8 = 4900 &= 2 \left[\text{—} \right]_{(2)} + 28 \left[\text{^} \right]_{(6)} + 32 \left[\text{^} \right]_{(18)} + 72 \left[\text{>} \right]_{(4)} + 8 \left[\text{zigzag} \right]_{(50)} \\
 &\quad + 16 \left[\text{zigzag} \right]_{(36)} + 48 \left[\times \right]_{(1)} + 264 \left[\square \right]_{(1)} + 112 \left[\square \right]_{(8)} + 16 \left[\square \right]_{(16)} \\
 &\quad + 16 \left[\square \right]_{(8)} + 16 \left[\square \right]_{(24)} + 32 \left[\square \right]_{(4)} + 96 \left[\text{hexagon} \right]_{(2)} + 16 \left[\text{hexagon} \right]_{(20)} \\
 &\quad + 48 \left[\square \right]_{(2)} + 32 \left[\square \right]_{(2)} + 16 \left[\text{hexagon} \right]_{(7)}
 \end{aligned}$$

(b) Simple cubic lattice

$$\begin{aligned}
 r_2 = 6 &= 2 \left[\text{—} \right]_{(3)} \\
 r_4 = 90 &= 2 \left[\text{—} \right]_{(3)} + 4 \left[\text{^} \right]_{(15)} + 8 \left[\square \right]_{(3)} \\
 r_6 = 1860 &= 2 \left[\text{—} \right]_{(3)} + 12 \left[\text{^} \right]_{(15)} + 6 \left[\text{^} \right]_{(75)} + 12 \left[\text{>} \right]_{(20)} + 48 \left[\square \right]_{(3)} \\
 &\quad + 12 \left[\square \right]_{(48)} + 12 \left[\text{hexagon} \right]_{(22)} \\
 r_8 = 44730 &= 2 \left[\text{—} \right]_{(3)} + 28 \left[\text{^} \right]_{(15)} + 32 \left[\text{^} \right]_{(75)} + 72 \left[\text{>} \right]_{(20)} + 8 \left[\text{zigzag} \right]_{(363)} \\
 &\quad + 16 \left[\text{zigzag} \right]_{(300)} + 48 \left[\times \right]_{(15)} + 264 \left[\square \right]_{(3)} + 112 \left[\square \right]_{(48)} + 16 \left[\square \right]_{(192)} \\
 &\quad + 16 \left[\square \right]_{(96)} + 16 \left[\square \right]_{(240)} + 32 \left[\square \right]_{(72)} + 96 \left[\text{hexagon} \right]_{(22)} + 16 \left[\text{hexagon} \right]_{(492)} \\
 &\quad + 48 \left[\square \right]_{(18)} + 32 \left[\square \right]_{(30)} + 16 \left[\text{hexagon} \right]_{(207)}
 \end{aligned}$$

- (c) *Combinatorial factors* (which represent the total number of returns to the origin having the given configurational pattern, these returns being summed over all vertices of the configuration)

$$\begin{array}{c} r_1 \\ \equiv \\ \equiv \\ \equiv \end{array} \quad \begin{array}{c} r_2 \\ \equiv \\ \equiv \\ \equiv \end{array} \quad \begin{array}{c} r_3 \\ \equiv \\ \equiv \\ \equiv \end{array} \quad l \frac{(r_1+r_2-1)!(r_2+r_3-1)!}{r_1!r_2!(r_2-1)!r_3!}$$

$$l = 2(r_1 + r_2 + r_3)$$

$$r_1 \begin{array}{c} r_2 \\ \equiv \\ \equiv \\ \equiv \end{array} \begin{array}{c} p \\ \equiv \\ \equiv \\ \equiv \end{array} \begin{array}{c} s_1 \\ \equiv \\ \equiv \\ \equiv \end{array} s_2 \quad l \frac{(p+r_1+r_2+r_3-1)!(p+s_1+s_2+s_3-1)!}{r_1!r_2!r_3!p!(p-1)!s_1!s_2!s_3!}$$

$$l = 2(r_1 + r_2 + r_3 + p + s_1 + s_2 + s_3)$$

$$\begin{array}{c} r_1 \\ \equiv \\ \equiv \\ \square \end{array} \quad \begin{array}{c} r_2 \\ \equiv \\ \equiv \\ \equiv \end{array} \quad \begin{array}{c} r_3 \\ \equiv \\ \equiv \\ \equiv \end{array} \quad 2l \frac{(r_1+r_2)!(r_2+r_3-1)!}{r_1!r_2!(r_2-1)!r_3!}$$

$$l = 2(r_1 + r_2 + r_3) + 4.$$

APPENDIX II

r_l AND q_l FOR SIMPLE LATTICES

Generating functions $\phi(x, y, z)$. (r_l is the coefficient independent of x, y, z in $[\phi(x, y, z)]^l$)

Simple quadratic

$$\phi = \frac{1}{4}(x^{-1} + x + y^{-1} + y),$$

$$r_l = (l!)^2 / [(\frac{1}{2}l)!]^4 \quad (l \text{ even}).$$

Triangular

$$\phi = \frac{1}{6}(x^{-1} + x + y^{-1} + y + xy^{-1} + x^{-1}y),$$

$$r_l = \sum_{s,t} \frac{1}{s!t!} \sum_{q=0}^s 2^{s-q} \frac{(t+q)!}{[(t+q)/2!]^2} \frac{1}{q!(s-q)!},$$

$$s, t = 0, 1 \dots l; \quad (2s+t) = l; \quad (t+q) \text{ even}.$$

Simple cubic

$$\phi = \frac{1}{6}(x^{-1} + x + y^{-1} + y + z^{-1} + z),$$

$$r_l = \sum_{r,s,t} \frac{l!}{(r!)^2(s!)^2(t!)^2}, \quad r, s, t = 0, 1 \dots \nu, \quad r+s+t = \nu, \quad l = 2\nu \text{ (even)}.$$

Body-centred cubic

$$\phi = \frac{1}{8}(x^{-1} + x)(y^{-1} + y)(z^{-1} + z),$$

$$r_l = (l!)^3 / \{(\frac{1}{2}l)!\}^6 \quad (l \text{ even}).$$

Face-centred cubic

$$\phi = \frac{1}{12}[(y^{-1}+y)(z^{-1}+z) + (z^{-1}+z)(x^{-1}+x) + (x^{-1}+x)(y^{-1}+y)],$$

$$r_l = \sum_{r,s,t} \frac{l!}{r!s!t!} \frac{(r+s)!}{[(\frac{1}{2}(r+s))!]^2} \frac{(s+t)!}{[(\frac{1}{2}(s+t))!]^2} \frac{(r+t)!}{[(\frac{1}{2}(r+t))!]^2}, r+s+t=l,$$

$r, s, t = 0, 1 \dots l, \quad r, s, t \text{ all odd or all even.}$

Honeycomb†

$$\phi = (1+x^{-1}+y^{-1})^{1/2}(1+x+y)^{1/2}, \quad r_l = \sum_{r,s,t} \frac{[(l/2)!]^2}{(r!)^2 (s!)^2 (t!)^2}$$

$l \text{ even } r+s+t=l/2.$

Diamond†

$$\phi = [(x+x^{-1}+z(y+y^{-1}))^{1/2}[(x+x^{-1}+z^{-1}(y+y^{-1}))^{1/2}]$$

$$r_l = [(l/2)!]^2 \sum_{s=0}^{l/2} \frac{(2s)!(l-2s)!}{(s!)^4 [(l/2-s)!]^4}$$

$l \text{ even.}$

Hexagonal close-packed. See § 5.2.8. r, q , as for face-centred cubic.

NUMERICAL VALUES OF r_p, q_l FOR SIMPLE LATTICES

Loose-packed lattices

	Honeycomb	S.Q.	Diamond	S.C.	B.C.C.
r_2	3	4	4	6	8
r_4	15	36	28	90	216
r_6	93	400	256	1860	8000
r_8	639	4900	2716	44730	343000
r_{10}	4653	63504	31504	1172556	16003008
r_{12}	35169	853776	387136	32496156	788889024
q_2	0	0	0	0	0
q_4	0	8	0	24	96
q_6	6	24	24	264	1776
q_8	0	216	48	4584	67584
q_{10}	30	1520	480	88560	2455200
q_{12}	66	12080	3432	1750800	94735920

Close-packed lattices

	Triangular	F.C.C. (or H.C.P.)		Triangular	F.C.C. (or H.C.P.)
r_2	6	12	q_2	0	0
r_3	12	48	q_3	12	48
r_4	90	540	q_4	24	264
r_5	360	4320	q_5	60	1680
r_6	2040	42240	q_6	444	17016
r_7	10080	403200	q_7	1680	151872
r_8	54810	4038300	q_8	7464	1401720
r_9	290640	40958400	q_9	35040	13238400

† These non-Bravais lattices require special treatment. The generating functions quoted will give r_l correctly.

APPENDIX III

TABLE A

Lattice constants of closed configurations

(† denotes irreducible configuration)














	Constant $\sigma = q - 1$	Triangular 5	Face-centred cubic 11	CP(6) 4	CP(7) 5
p_3^\dagger		2	8	10/3	5
p_4^\dagger		3	33	15/2	15
p_5^\dagger		6	168	12	36
p_{5a}		3	36	15	30
p_6^\dagger		15	970	10	60
p_{6a}^\dagger		0	36	10	30
p_{6b}		12	384	60	180
p_{6c}		9	204	15	45
p_{6d}^\dagger		0	2	5/2	5
p_7^\dagger		42	6168	0	360/7
p_{7a}		12	966	30	180
p_{7b}		30	2400	60	360
p_{7c}		6	192	60	180

TABLE A (*continued*)














	Constant	Triangular	Face-centred cubic	CP(6)	CP(7)
p_{7d}		42	2196	15	90
p_{7e}		30	2040	30	180
p_{7f}^\dagger		0	600	30	180
p_{7g}		0	24	10	30
p_{7h}^\dagger		0	48	30	90
p_{8i}^\dagger		123	42069	0	0
p_{8a}		96	16464	0	360
p_{8b}		60	11616	0	360
p_{8c}^\dagger		6	3888	0	180
p_{8d}^\dagger		3	3132	0	180
p_{8e}		24	2016	120	720
p_{8f}		12	1056	60	360
p_{8g}		66	12096	0	180

Table A (*continued*)














	Constant	Triangular	Face-centred cubic	CP(6)	CP(7)
p_{8h}		24	4968	0	90
p_{8j}		144	22176	0	180
p_{8k}		186	22632	0	90
p_{8l}		12	1032	30	180
p_{8m}		18	1176	30	180
p_{8p}		0	528	60	360
p_{8q}		0	24	30	90
p_{8r}^\dagger		0	9	5/2	15
p_{8s}		0	384	30	180
$p_{9\dagger}$		380	301376	0	0
p_{9a}		180	79920	0	0
p_{9b}		102	58032	0	0
p_{9c}		48	6432	0	90

TABLE A (continued)














	Constant	Triangular	Face-centred cubic	CP(6)	CP(7)
p_{9d}		2	744	0	15
p_{9e}		0	2352	0	180
p_{9f}		0	1848	0	180
p_{9g}		2	160	20	120
p_{9h}^\dagger		0	192	0	60
	Constant $\sigma = q - 1$	Simple quadratic 3	Simple cubic 5	Body-centred cubic 7	LP(8) 3
p_4^\dagger		1	3	12	9/2
p_6^\dagger		2	22	148	12
p_{6a}^\dagger		0	0	12	6
p_{7a}		2	18	192	36
p_8^\dagger		7	207	2736	9
p_{8c}^\dagger		0	24	480	36
p_{8h}		2	30	618	18
p_{8r}^\dagger		0	0	3	3/2

TABLE A (*continued*)










	Constant	Simple quadratic	Simple cubic	Body-centred cubic	LP(8)
p_{8t}^\dagger		0	0	24	18
p_{9j}		8	192	4632	18
p_{9k}		12	324	6576	72
p_{9l}^\dagger		0	20	436	12
p_{9m}		0	0	456	72
p_{10}^\dagger		28	2412	61896	0
p_{10a}		8	576	19584	0
p_{10b}		0	12	304	12
p_{10c}^\dagger		0	0	120	0

TABLE B

Lattice constants of open configurations

		Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
1·1		2	3	3	4	6
2·1		6	15	15	28	66
3·1		4	20	20	56	220
3·2		18	69	75	196	702
4·1		0	24	0	0	240
4·2		1	15	15	70	495
4·3		36	252	300	1176	6780
4·4		50	309	363	1324	7350
5·1		8	42	48	288	1248
5·2		0	90	0	0	2328
5·3		0	36	0	0	1080
5·4		0	108	0	0	2496
5·5		0	6	6	56	792

TABLE B (continued)


















		Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
5·6		12	228	300	1960	19620
5·7		18	207	300	1764	15786
5·8		92	1104	1404	7656	69924
5·9		100	1020	1452	7944	68508
5·10		142	1365	1767	8980	76266
6·1		0	96	0	0	7632
6·2		0	24	0	0	696
6·3		0	18	0	0	648
6·4		8	75	96	828	5808
6·5		16	132	192	1728	11400
6·6		4	54	72	720	5292
6·7		24	186	240	1944	12744
6·8		0	104	0	0	7296

TABLE B (continued)

		Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
6·9		0	252	0	0	20304
6·10		0	24	0	0	2880
6·11		0	792	0	0	47760
6·12		0	192	0	0	11784
6·13		0	288	0	0	21648
6·14		0	480	0	0	25872
6·15		0	1	1	28	924
6·16		0	102	150	1960	37800
6·17		12	330	600	5880	87948
6·18		38	966	1308	10656	163926
6·19		184	3240	5616	45936	627912
6·20		520	8796	13656	103872	1400328
6·21		268	4836	6876	52152	719748

TABLE B (*continued*)

		Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
6-22		84	1312	2260	17240	226780
6-23		28	984	1356	12280	199476
6-24		50	1242	2178	19860	286638
6-25		390	5973	8463	60028	786858

Lattice constants of open configurations (simple chains)

The values of c_l , the total number of non-intersecting chains of l lines, for various lattices.











	Simple quadratic	Triangular	Simple cubic	Body-centred cubic	Face-centred cubic
c_1	2	3	3	4	6
c_2	6	15	15	28	66
c_3	18	69	75	196	702
c_4	50	309	363	1324	7350
c_5	142	1365	1767	8980	76266
c_6	390	5973	8463	60028	786858
c_7	1086	25941	40695	402412	8086074
c_8	2958	112065	193983	2675860	82848522
c_9	8134	482067	926943	17826340	—
c_{10}	22050	2066583	—	—	—
c_{11}	60146	—	—	—	—
c_{12}	162466	—	—	—	—
c_{13}	440750	—	—	—	—
c_{14}	1187222	—	—	—	—
c_{15}	3208298	—	—	—	—
c_{16}	8622666	—	—	—	—

TABLE C

Separated configurations. (To avoid fractions we tabulate $l!$ (coefficient of N) where l is the number of lines)

	Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
//	-14	-33	-33	-60	-138
^/	-360	-1404	-1440	-3696	-13320
///	+232	+864	+876	+2192	+7752
Δ/	0	-720	0	0	-6336
^/	-1248	-9504	-10080	-38976	-231840
^/	-5520	-33336	-37512	-135264	-743472
^//	+13872	+85176	+90072	+319392	+1766736
////	-6252	-36846	-38286	-132456	-720756
^ ^	-2976	-19260	-20556	-74688	-421920
□/	-1440	-6840	-7200	-40320	-169920
Δ/	0	-56160	0	0	-1249920
×/	-1920	-42480	-46800	-302400	-3196800
^/	-67200	-732960	-924480	-5011200	-44144640

TABLE C (*continued*)

	Simple quadratic	Triangular	Simple cubic	Body- centred cubic	Face- centred cubic
	-94080	-913680	-1121040	-5650560	-48113280
	0	+53280	0	0	+1036800
	+68640	+812160	+908640	+4864320	+44160480
	+302160	+2883240	+3372840	+16829280	+142173360
	-677280	-6267840	-7201440	-35373120	-300739680
	+235488	+2197872	+2359152	+11313216	+94744224
	+327840	+3329280	+3705480	+18639360	+161395200
	0	-24480	0	0	-498240
	+24960	-317520	-354240	-1752960	-18123840
	+111840	-1119600	-1324080	-6106560	-58263840

Separated configurations required for the first nine terms of the Ising no-field series

$$[p_3, p_3] = Np_3^2/2 - (p_{6c} + p_{7a} + \frac{1}{2}p_3)$$

$$[p_3, p_4] = Np_3p_4 - (p_{7e} + 3p_{7g} + p_{6b} + 2p_{5a})$$

$$[p_4, p_4] = Np_4^2/2 - (p_{8h} + 3p_{8r} + p_{8s} + p_{7a} + p_{7c} + 3p_{6a} + 3p_{6d} + \frac{1}{2}p_4)$$

$$[p_3, p_5] = Np_3p_5 - (p_{8g} + 2p_{8s} + p_{7b} + p_{7c} + p_{6b})$$

$$[p_3, p_6] = Np_3p_6 - (p_{9a} + 2p_{9e} + p_{9f} + p_{9g} + p_{8a} + p_{8e} + p_{7b})$$

$$[p_4, p_5] = Np_4p_5 - (p_{9b} + p_{9c} + 2p_{9f} + 3p_{9g} + 3p_{9h} + p_{8b} + p_{8e} + 2p_{8p} + 2p_{8q} + 2p_{7f} + 2p_{7h} + p_{6b})$$

$$[p_3, p_{6c}] = Np_3p_{6c} - (2p_{9c} + 3p_{9d} + 3p_{9g} + 2p_{8l} + 2p_{8m} + 2p_{8q} + p_{7c} + 2p_{8c})$$














$$[p_3, p_3, p_3] = N^2p_3^3/6 - N(p_{6c}p_3 + p_{5a}p_3 + p_3^2/2) + (p_{9c} + 2p_{9d} + 2p_{9g} + 2p_{8l} + p_{8m} + 2p_{8q} + 2p_{7c} + 2p_{7g} + 2p_{6c} + 8p_{6d} + 2p_{5a} + p_3/3)$$

For loose-packed lattices we quote an additional term














$$[p_4, p_6] = Np_4p_6 - (p_{10a} + 3p_{10b} + 3p_{10c} + p_{9k} + 2p_{9m} + 2p_{8c} + 2p_{8l} + 2p_{7a}).$$

APPENDIX IV

Table of Low-temperature Configurations (Evaluated for $N=1$)

Configuration	Simple quadratic	Simple cubic	Body- centred cubic	Triangular	Face- centred cubic
	+1	+1	+1	+1	+1
	+2	+3	+4	+3	+6
	-2	-3	-4	-3	-6
P_3 	0	0	0	+2	+8
	+6	+15	+28	+9	+42
	-14	-33	-60	-27	-114
	+8	+18	+32	+16	+64
P_{6d} 	0	0	0	0	+2
P_{5a} 	0	0	0	+3	+24
P_4 	+1	+3	+12	0	+3
	0	0	0	+12	+120
	+14	+63	+148	+27	+282
	+4	+20	+56	+2	+44









APPENDIX IV.—*Table continued*

Configuration	Simple quadratic	Simple cubic	Body- centred cubic	Triangular	Face- centred cubic
	0	0	0	-22	-192
	-21	-81	-194	-57	-513
	-56	-228	-568	-108	-1080
	+98	+360	+868	+249	+2166
	-40	-137	-322	-106	-856
P_{8u} 	0	0	0	0	+6
P_{8q} 	0	0	0	0	+24
P_{7c} 	0	0	0	+6	+72
	0	0	0	0	+24
P_{6a} 	0	0	+12	0	0
	0	0	0	0	-54
P_{6b} 	0	0	0	0	+24
	0	0	0	+6	+168

APPENDIX IV.—*Table continued*

Configuration	Simple quadratic	Simple cubic	Body- centred cubic	Triangular	Face- centred cubic
	0	0	0	+12	+240
P_{6c}	0	0	0	+3	+72
	+8	+48	+216	0	+48
	0	0	0	+36	+792
	0	0	0	+24	+576
	0	0	0	0	+96
	0	0	0	-39	-696
	-11	-57	-288	0	-87
	0	0	0	-90	-1680
	0	0	0	-168	-3672
	+34	+267	+820	+81	+1902
	+20	+204	+672	+18	+828
	+1	+15	+70	0	+9

APPENDIX IV.—*Table continued.*

Configuration	Simple quadratic	Simple cubic	Body- centred cubic	Triangular	Face- centred cubic
	0	0	0	+ 222	+ 4080
	- 44	- 372	- 1360	- 30	- 1404
	- 166	- 1227	- 3860	- 405	- 9162
	- 160	- 1077	- 3536	- 441	- 9480
	+ 349	+ 2130	+ 6834	+ 1203	+ 22773
	+ 450	+ 2925	+ 9600	+ 1143	+ 23910
	- 706	- 4041	- 12852	- 2370	- 42366
	+ 225	+ 1185	+ 3672	+ 789	+ 12957

REFERENCES

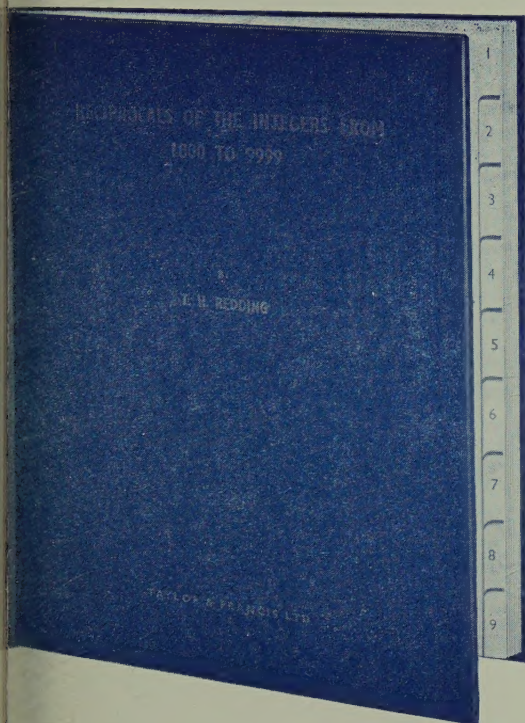
General References

- BERGE, CLAUDE, 1958, *Theorie Des Graphes et ses Applications* (Paris: Dunod).
 FORD, G. W., 1954, Thesis, University of Michigan.
 FORD, G. W., HARARY, F., NORMAN, R. Z., and UHLENBECK, G. E., 1956, *Proc. nat. Acad. Sci., Wash.*, **42**, 122, 203, 529; 1957, *Ibid.*, **43** 163.
 KONIG, D., 1936, *Theorie Der Graphen* Re-issued by Chelsea Publishing Company, New York 1950.
 RIDDELL, R. J., JR., 1951, Thesis, University of Michigan.
 RIDDELL, R. J., JR., and UHLENBECK, G. E., 1953, *J. chem. Phys.*, **21**, 2056.
 RIORDAN, JOHN, 1958, *An Introduction to Combinatorial Analysis* (New York: John Wiley).

References

- BROOKS, J. E., and DOMB, C., 1951, *Proc. roy. Soc. A*, **207**, 343.
BROWN, H. A., 1956, *Phys. Rev.*, **104**, 624.
BROWN, H. A., and LUTTINGER, J. M., 1955, *Phys. Rev.*, **200**, 685.
CAYLEY, A., 1889-98, Collected Works.
DOMB, C., 1949, *Proc. roy. Soc. A*, **199**, 199.
DOMB, C., and FISHER, M. E., 1958, *Proc. Camb. phil. Soc.*, **54**, 48.
DOMB, C., MARADUDIN, A. A., MONTROLL, E. W., and WEISS, G. H., 1959, *Phys. Rev.*, **115**, 18, 24.
DOMB, C., and SYKES, M. F., 1956, *Proc. phys. Soc., Lond. B*, **69**, 486; 1957 a, *Phil. Mag.*, **2**, 733; 1957 b, *Proc. roy. Soc. A*, **240**, 214; 1957 c, *Proc. phys. Soc., Lond. B*, **70**, 896.
FISHER, M. E., and SYKES, M. F., 1958, *Phys. Rev. Letters*, C.527-1-2; 1959, *Phys. Rev.*, **114**, 45.
GILLIS, J., 1955, *Proc. Camb. phil. Soc.*, **51**, 639.
HUSIMI, K., 1950, *J. chem. Phys.*, **18**, 682.
MANDL, F., 1954, *Quantum Mechanics*, Chapter VI.
OPECHOWSKI, W., 1937, *Physica*, **4**, 181, 1939, *Ibid.*, **6**, 1112.
RUSHBROOKE, G. S., and EVE, J., 1959 (private communication).
RUSHBROOKE, G. S., and SCOINS, H. I., 1955, *Proc. roy. Soc. A*, **230**, 74.
RUSHBROOKE, G. S., and WOOD, P. J., 1955, *Proc. phys. Soc., Lond. A*, **68**, 1161; 1957, *Ibid. A*, **70**, 765; 1958, *Mol. Phys.*, **1**, 257.
SYKES, M. F., 1956, Thesis, Oxford; 1960 (to be published).
TEMPERLEY, H. N. V., 1956, *Phys. Rev.*, **103**, 1; 1959, *Proc. phys. Soc., Lond.*, **74**, 183.
WAKEFIELD, A. J., 1951, *Proc. Camb. phil. Soc.*, **47**, 419; 1952, Thesis, Oxford.
YVON, J., 1945, *Cah. Phys.*, No. 28, 1948, *Ibid*, Nos. 31, 32.
ZEHLER, V., 1950, *Z. Naturf. A* **5**, 344.

FOR USERS OF CALCULATORS



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By T. H. Redding

M.Sc.(Lond.), A.M.I.Mech.E., A.F.R.Ae.S.

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With an Appendix on mechanical barrel-setting calculators

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Although suitable for general use, the tables have been prepared and arranged in a manner particularly suitable for use in conjunction with mechanical computing machines of the "barrel-setting" type in the evaluation of quotients and compound fractions. Equally the tables find application in effecting the evaluation of quotients on adding and listing machines when these incorporate a mechanism for automatically evaluating simple products.

In the first instance it was anticipated that an Appendix dealing with the advantages to be gained by the use of the reciprocal function in conjunction with such machines—and particularly with barrel-setting machines—would suffice to ensure the best use being made of the tables. The present 22-page *Appendix*, however, goes further than this, since the discussion of the tables is prefaced by a description of barrel-setting machines and their (simplest) method of operation in the evaluation of products, quotients and compound fractions. Thus, the description of each calculating procedure is followed by a numerical example with accompanying diagrams to illustrate the keyboard-displays at the beginning, the end, and at intermediate stages in the calculation. The machine-evaluation of series comprising the sum of a number of product or quotient-terms is also discussed. Generally it is hoped that the *Appendix* will serve as an introduction to mechanical methods of computation and that it will materially assist prospective purchasers in the choice of a machine.

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